THE OLIGOMERIZATION OF PROPENE OVER COBALT CATALYSTS

By

Paul Michael Dickens
BSc (Chem Eng) (Natal)

Submitted to the University of Cape Town in fulfilment of the requirements for the degree of Master of Science in Engineering.

SYNOPSIS

This thesis set out to investigate the activity of various supported cobalt catalysts for high pressure propene oligomerization. This work was carried out as part of a larger research effort to upgrade light olefins to liquid fuels in the distillate range. The supports investigated included activated carbon, alumina, silica alumina, synthetic mica montmorillonite, zeolite Y and NH_4^+-ZSM-5. A cobalt-molybdenum hydrodesulphurization catalyst was also tested. The synthesis procedures used in this work included double ammoniation (Co-C), incipient wetness impregnation (Co-C, alumina, NH_4^+-ZSM-5), ion-exchange (NaY, NH_4^+-ZSM-5), chemisorption (cobalt complex on activated carbon) and homogeneous deposition-precipitation (Co-Silica alumina).

A high pressure integral reactor (volume = 25ml), immersed in a fluidised sand bath to facilitate isothermal operation, was constructed. Catalysts were calcined either in ultra-high purity nitrogen or in air. The oligomerization reaction was carried out at 50 atm(g) and at temperatures varying from ambient to 380°C.

The best double ammoniated Co-C catalyst (13 wt % CoO supported on Copcarb WCM 106 activated carbon) produced 66g of liquid per gram of catalyst with an average conversion of 46% under conditions of a average WHSV of $12,5\pm0,5h^{-1}$ and reaction temperature of 40°C. The selectivity to dimer was 80-85%. Four-fold reductions in liquid production resulted from a reaction temperature increase of 30°C and by the use of industrial nitrogen (4500ppm O_2) as opposed to ultra-high purity nitrogen (3vpm O_2) during the calcination.

Both a cobalt-carbon interaction and adequate ammoniation were essential for activity. The role of the ammonia treatments was not conclusively resolved. The ammoniation of the raw activated carbon (pre-ammoniation) is believed to improve cobalt adsorption onto the activated carbon and enhance the resultant dispersion. The ammoniation subsequent to cobalt loading (post-ammoniation) was believed either to improve dispersion or

to create a dynamic active site (or site precursor). The effect of post-ammoniation was found to be a function of contact time. A 1h period of post-ammoniation approached the optimal treatment. A proposed cobalt(III) hexaammine complex site precursor was synthesized and found to be inactive. The surface of the activated carbon was modified by treatments with O_2, HNO_3 and HF in an attempt to elucidate the interaction between the cobalt and the activated carbon. It was hypothesized that oxygen functional groups played an important role in this interaction and this work did not refute this hypothesis.

Control experiments were undertaken with the acidic aluminosilicate supports (silica alumina, SMM, NH_4^+-ZSM-5). The cobalt modified supports were then tested for low temperature activity, promoting effects and selectivity changes in the acid catalyzed reaction. Only cobalt-silica alumina (12,1 wt % Co) showed low temperature activity (70°C) for which the cobalt was responsible. At a WHSV of $6,2h^{-1}$ a maximum conversion of 19% was obtained. The product consisted predominantly of trimer (58%). No additional work was carried out to optimise this catalyst formulation.

Cobalt ion-exchanged into SMM and NH_4^+-ZSM-5 caused a reduction in activity of the acid catalyzed reactions. A significant finding of the ZSM-5 run was the marked reduction of cracking at 280°C by the introduction of cobalt. This was believed to have been the result of a loss of the strongest acid sites through the ion-exchange. The protonated form of zeolite Y proved to be an unsuccessful support due to rapid deactivation. An ammoniated 41% ion-exchanged Co(II)NaY catalyst showed slight activity (a 15% conversion for 1h with a WHSV of $6h^{-1}$ and a temperature of 180°C). The cause of this activity remained unclear.

The cobalt impregnated NH_4^+-ZSM-5 and alumina catalysts experienced reduced activity and no activity, respectively. The reduced activity of the NH_4^+-ZSM-5 catalyst was ascribed to cobalt crystallites blocking pores and reducing access to both the surface and pore acid sites.

The general conclusion of this work was that cobalt requires specific co-ordination ligands to become active and that the usual interactions through ion-exchange with or impregnation onto an aluminosilicate support did not satisfy this requirement. The catalytic potential of cobalt when correctly co-ordinated was clearly evident from the double ammoniated cobalt-carbon catalyst.

ACKNOWLEDGEMENTS

It has been my privilege to have been associated with the following people:

Dr. M. Kojima and Prof. C.T. O'Connor whose guidance and support was sincerely appreciated;
Deaghlin McClean, Klaus Moller, Lester Jacobs, Stefan Harms, Stephan Schwarz, Alex Vogel and Bo Anderson - your friendship and help smoothed many a difficult moment;
Messrs. Barker, Senekal and Randall - for excellent technical assistance;
The entire Chemical Engineering Staff.

SASOL and the Council for Scientific and Industrial Research are gratefully acknowledged for financial assistance.

Stephan Schwarz is acknowledged for synthesis of the ZSM-5 support used in this work.
Prof. Willis of Geochem. (UCT) is acknowledged for XRF analysis.
Granville De La Cruz is thanked for his assistance with the printing and binding of this thesis.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 3

NOMENCLATURE

τ-alumina	Gamma alumina.
A.A.	Atomic absorption.
Catalysts:	
Co-C	Cobalt supported on activated carbon - a generalised term for all versions of such catalysts.
Co-OC	The oxygen treated activated carbon version of Co-C.
Co-HFC	Hydrofluoric acid treated activated carbon.
Co-C1hA	Double ammoniated carbon supported catalyst wih a 1h post-ammoniation.
CoOCSPn	Cobalt oxide on activated carbon Schultz Patent attempt number n - a series of 5 catalysts synthesized in an attempt to reproduce the catalyst due to Schultz et al. (1966a).
Co-Si/Al	Cobalt supported on silica alumina.
Co(II)NaY	Cobalt ion-exchanged into zeolite Y.
Co-NH_4^+-ZSM-5	Cobalt supported on protonated ZSM-5.
CI	Cracking Index.
F.I.D.	Flame ionization detector.
G.C.	Gas chromatograph.
G.C./M.S.	Gas chromatography/ Mass spectrophotometry.
HPN_2	High purity nitrogen.
Isomers:(eg.)	
2M1P	2-methylpent-1-ene.
1H	Hex-1-ene.
LP	Liquid production (g prod / g cat).
Si/Al	Silicon to aluminium mole ratio.
SV	Space velocity (g feed/ h).
WHSV	Space velocity (g feed /h·g cat).
$UHPN_2$	Ultra-high purity nitrogen.
U.V.	Ultra violet spectrophotometer.

1 INTRODUCTION

South Africa is a country of vast mineral resources and industrial potential. An important criterion for the realization of this potential is the availability of energy sources. Coal reserves have been estimated to be of the order of +90Gt (Ion, 1976) but South Africa has as yet discovered insignificant quantities of natural liquid fossil fuels. In the light of the invention of the Fischer - Tropsch process, it was a logical strategy to convert some of the coal reserves into liquid fuels.

Over the last four decades, the South African Coal, Oil and Gas Corporation (SASOL) has been producing synthetic fuels. Current production is of the order of 70 thousand barrels per day (Dutkuwicz, 1980). The typical fractions of petrol and diesel from their Synthol reactors has been 39,0% and 5,0% respectively (Jager, 1978). 10% of the product is also made up of propene and butenes. It is the above two factors which form the basis for the motivation of the research undertaken in this thesis. Firstly, the 10% gas stream is in excess of market requirements and as such is a low value product. Secondly the market requires approximately equal quantities of petrol and diesel. The imbalance between petrol and diesel requires rectification.

This thesis forms part of a larger research effort to produce a diesel fraction (linear hydrocarbons in the range C_{12} to C_{18}) via the oligomerization of propene. Thermodynamics dictates that branched products would be the favoured species in an oliomerization reaction. A catalyst system must be found or engineered to produce the desired linear products.

1.1 The Selection of Cobalt as an Oligomerizing Catalyst

In approaching the problem of oligomerization, either acidic or basic catalysts may be considered. Little is reported in the literature on basic systems and the acid catalyzed route is generally preferred. Acid catalysts have both the advantages and disadvantages of promoting many

reactions: isomerization, polymerization, cracking and cyclicization, to mention a few. The extent of these competing reactions depends on the temperature and pressure of operation.

Within the catagory "heterogeneous acid catalysts", there are three divisions: i) protonic acids, e.g., silicophosphoric acid; ii) acidic oxides, e.g., aluminosilicates which have both Bronsted and Lewis acid sites; iii) supported metal catalysts. Not only is silicophosphoric acid well researched by also its selectivity toward linear products is low. The aluminosilicates still require much research but at present it would appear that high temperatures are necessary (Occelli et al., 1985; Harms, 1987). Under such conditions, cracking and coking become important and linear product selectivity is reduced through isomerization. Metal supported catalysts show greater promise in terms of selectivity, at least as far as the dimer is concerned.

TABLE 1.1: Performance of heterogeneous cobalt and nickel catalysts.

Catalyst	Co-Activated Carbon	Ni-Silica Alumina
Mass(g)	9	-
Temperature(°C)	30-66	70
Pressure(atm)	50	40
Time(h)	222	-
Product(g)	605	-
% hexenes	95	72
% n-Hexenes	55	35
Reference	Schultz et al. (1966a)	Hogan (1955)

Cobalt oxide supported on activated carbon has been found to be active for propene dimerization at room temperature. Nickel oxide on silica alumina is active at 75°C. Table 1.1 gives typical performances. The cobalt catalyst was clearly more selective to dimer. Two homogeneous analogues of cobalt and nickel gave a reversed trend (Table 1.2).

TABLE 1.2: Performance of homogeneous cobalt and nickel catalysts.

Catalyst	$CoCl_2$:$AlEt_2Cl$:CH_2Cl_2	$Ni(acac)_2$:$AlEt_2Cl$:Ch_2Cl_2
Mass (g)	2,6:4,8:15	2,6:4,7:20
Temperature(°C)	40-66	40
Pressure (atm)	41	42
Time(h)	4	17
Product(g)	182	110
% Hexenes	31	95
% n-Hexenes	33	28
Reference	Jones (1971)	Jones (1971)

The above two tables suggest that both cobalt and nickel have the ability to catalyze either highly selective dimerization reactions or longer chain oligomerization reactions. The important criterion was the environment in which the metal was placed. It is thus deemed possible that the selectivity of the metal supported catalysts could be improved. The first alternative is to attempt to upgrade the oligomerization reaction to produce polymer in the diesel range. Secondly, the production of a highly linear dimer could be optimised. This would prove a valuable feed stock for further dimerization to at least a fairly linear tetramer. What is in effect being proposed is a two or more step process whereby conditions may be optimised at each stage improving the overall selectivity to linear products.

Cobalt is selected as the metal for research because of the following factors:

* the performance of cobalt displayed in homogeneous polymerization (Table 1.2);
* the potential suggested by the cobalt on activated carbon system (Table 1.1);
* in Fischer Tropsch synthesis, cobalt is well known to produce longer chain hydrocarbons (Pines, 1981);
* the chemical similarity of cobalt and nickel.

At present, little is understood about the metal support interaction and the catalytic interaction between the hydrocarbon and the metal or metal oxide. It is hoped that, in investigating cobalt on various well known supports, some understanding of these various interactions may emerge.

1.2 Supported Cobalt Catalysts: Cobalt on Activated Carbon

The catalyst synthesized by supporting cobalt oxide on activated carbon has been found to exhibit the ability predominantly to dimerize propene, ethene and other α-olefins. All workers agree that simply impregnating cobalt on activated carbon does not produce a catalyst of significant activity. However, the procedures developed by these workers to synthesize active catalysts are often contradictory. For this reason, a detailed comparative study is given below.

1.2.1 Catalyst Preparation

1.2.1.1 The Carbon Support Phase

Activated carbon can be synthesized from many different sources. Workers have found that different source materials give differing catalyst activities. In their patent literature, Addy and Hill (1968, a and b) used both coal and nut charcoal activated carbons. No particular comments are made on these choices or on any pretreatments except that the carbon source be preferably steam treated up to 1200°C. Schultz et al. (1966a) on the other hand found that coke was the most active support. Wood, coconut and pecan shell were also tested. Product spectra were similar but activities varied greatly. No comment was made as to the atmospheres in which the various carbons were activated. No conclusion could thus be drawn as to the nature of the carbon surface. It could be possible that the activation procedure is more important than the starting material (See 1.3).

Schultz et al. (1966a) found that the ash content was an important variable and for maximum activity, the sum of cobalt oxide and ash

contents should be 13 wt%. In their documented runs Schultz et al. (1966a) reduced the ash content of their carbon by three successive leachings with aqueous HF (48%) from 5,5 wt% to 0,38 wt% ash. No reference was made as to what effect the ash content had on catalyst lifetime or on relative activity. This strong acid treatment could have changed the nature of the carbon surface and in effect modified the adsorptive and catalytic properties of the surface. The effect of the HF pre-wash was not discussed beyond ash content reduction. The workers of Dutch patent 6412392 also reduced the ash content of their coconut shell activated carbon to less than 1% using nitric acid.

1.2.1.2 The Choice of Metals

Schultz et al. (1966a) found that no other cobalt salt matched the nitrate for effectiveness. Further, only those salts which decomposed to the oxide were active. When other metals were co-loaded, it was found to be necessary to load the cobalt second. No other metal was active when supported alone on the carbon (These generalised statements were not substantiated and the effect of a co-loaded metal was not reported). Addy and Hill (1968b) reported that any cobalt salt could be used as long as another nitrate salt was co-loaded (eg., $Cu(NO_3)_2$). It was imperative that the cobalt be loaded before the nitrate decomposition step took place. They found the following necessary conditions for the total nitrate content: the ratio of gram ions of nitrate ions to gram atoms of cobalt must be greater than 2:1 and that the total nitrate must be 20-40% by mass (based on carbon). The nitrate specification is supported by the Schultz et al. (1966a) value of 26 wt% (which corresponds to the 13 wt% CoO on the activated catalyst). In contradiction, Hill (1969) invented an active catalyst requiring no nitrate ions. It was necessary to use cobalt and another ion, typically copper or nickel. For the case of a preferred copper amine salt, it was important to impregnate the cobalt first. It is important to note that the above two British patented catalysts had totally different activation procedures (1.2.1.4).

The ranges of metal loadings were as follows (all relative to the mass of carbon used): Schultz et al. (1966a) specified a total oxide content (CoO + ash) of 13% by mass; Hill (1969) gave a minimum metal content of 10 wt% (with at least one other metal atom per cobalt atom) and Addy and Hill (1968b) suggested 5-10 wt% cobalt.

1.2.1.3 Catalyst Synthesis

All workers have used simple impregnation as the technique of loading the metals onto the carbon support. There seems to be no real preference of solvent used. The only important criteria were that the solvent should be able to be driven off at low temperatures (100°C or less) and that the salts used be soluble in the solvent. On account of the high adsorptivity of activated carbon, proportions of solvent to carbon were chosen by Schultz et al. (1966a) to give incipient wetness or pore volume impregnation. Notable is the fact that no surface analysis has been undertaken to measure the degree of dispersion. This could be due to interference of the carbon support in surface analysis techniques.

Unique to the synthesis of Schultz et al. (1966a) was the pre- and post-impregnation soaking of the carbon with ammonia solution. After each of the above treatments, the carbon was dried at 120°C on a hot plate and then vacuum dried at 120°C and 100mmHg for 18-25h. Schultz et al. (1966a) did not explain the purpose of the pre-ammoniation. It is possible that the ammonia modifies the carbon surface functional groups improving its ability to adsorb the cobalt salts. This would give better dispersion.

In USP 3333016, Schultz discussed an alternative procedure for the pre-impregnation ammonia treatment. The activated carbon was pretreated by heating to temperatures in the range 200-300°C in flowing H_2, N_2 or N_2/H_2. The pressure should be reduced to 20-100 mmHg for safety reasons. Contact time could vary from 1 to 5h. The optimum conditions would depend on the contacting system used. After any H_2 treatments, the catalyst had to be flushed with N_2 before cooling.

1.2.1.4 Catalyst Activation

There are two fundamental activation conditions reported in the literature. The choice of activation condition depended on the presence or absence of a nitrate salt. Where nitrates were present, it was always necessary to activate the catalyst in inert atmospheres with nitrogen being preferred. Partial vacuums have also been advocated. Such catalysts were oxygen sensitive and had to be protected from air at all times after activation. In the case where salts other than nitrates were used, Hill (1969) activated his catalyst in a nitrogen gas containing molecular oxygen. The rate of oxygen addition had to be carefully controlled due to the highly exothermic reaction which could result in excessive hot-spots and consequent catalyst deactivation. In order for the catalyst to be active, it had to be flushed with an inert gas (typically N_2) before cooling to reaction temperature. This was done after no further nitrogen compounds were observed in the flue gas.

The choice of activation temperature was important. Schultz et al. (1966a) found that heating to 200-275°C in 35 mmHg vacuum with a nitrogen bleed gave an active catalyst, the optimum temperature being 275°C. The conversion increased monotonically to ca. 275°C before diminishing. If heated above 275°C, an isomerization function was initiated. This function was characterised by the appearance of 2-methylpent-2-ene in the polymer product. Addy and Hill (1968b) indictated that temperatures should be hot enough to decompose the chosen nitrate (typically between 250-500°C). However, they did not indicate what effect activation temperature had on their catalyst, other than the fact that hot spots caused deactivation.

Schultz et al. (1966a) showed that the period of activation had an optimum and that calcining for extended periods deactivated the catalyst (Fig. 1.1). This phenomenon was explained by a thermal degradation of sites. It was possible that trace quantities of oxygen (invariably present in N_2) could have resulted in a cumulative deactivation effect.

All catalysts activated in reducing atmospheres (eg., H_2, CO) were found to reduce activities. Schultz et al. (1966a) also observed an increased isomerizing capability for their catalyst activated in H_2.

It should be noted that the thermal decomposition of a nitrate on activated carbon is potentially explosive. Workers found that $Co(NO_3)_2$ was less stable than other metal salts and hence they investigated using other salts as starting materials. It is unfortunate that ammonium nitrate is so thermally unstable as this compound contains ions which both Schultz et al. (1966a) and Addy and Hill (1968b) considered to be crucial. Schultz et al. (1966a) did not report any risks involved in their synthesis and calcination procedures. Addy and Hill (1968b) developed a heating tube into which the nitrated catalyst was slowly fed against a stream of N_2 at 250°C, the principle of this technique being that hot spots could not develop; individual particles should not be able to generate enough heat. It is surprizing that this temperature shocked catalyst was still active. The presence of copper ions could well be responsible for maintaining dispersion and activity. They noted that a catalyst prepared in this manner but without the copper was practically inactive.

1.2.1.5 The Use of Promoters

The only promoter reported in the literature is that of Addy and Hill (1968a). They took a typical carbon supported cobalt catalyst which had been activated by nitrate decomposition. The catalyst was then heated in molten sodium or potassium at temperatures just above the liquification point of the metal (120-180°C). Air and water were excluded. An alternative procedure was to add the alkali metal to the feed. The catalyst activity was significantly promoted although the life time was not reported (see 1.2.2.5).

1.2.2 Trends Determined by Batch Experiments

In US Patents 3317628 and 3333016 Schultz and co-workers presented a large number of results, generated in batch reactors. These were useful

for obtaining qualitative information. Other workers have also generated batch run data but direct comparison between their work was difficult because no standard experimental procedure was adopted. The most significant difference was that Addy and Hill (1968b) ran batches for 1h compared to the 5h by Schultz and co-workers. A further criticism is that complete data was not given for all runs and comparison between the different sets of comparative data was often impossible.

1.2.2.1 The Effect of Ammonia Treatments

Using the standard synthesis procedure reported by Schultz et al. (1966a), the following activities (USP 3317628) were generated at 85°C and corresponding propene saturation pressure with run times of 5h (conversion data not available):

TABLE 1.3: The effect of pre- and post-ammoniations.

Catalyst	g prod/g cat
CoO/C	8,02 (ave of 18 runs)
CoO/B-C*	13,04 (ave of 11 runs)
B-CoO/B-C**	28,50 (ave of 10 runs)

*...B-C implies activated carbon pretreated with ammonia.
**...B-CoO implies catalyst post ammoniated

Different ammoniating procedures were also investigated. Ammonia gas (90 ml/min) was passed over carbon at 275-300°C and at pressures of 35-50 mmHg for 2-5h. After cooling under N_2, the cobalt was impregnated and the catalyst activated in the usual way. The following comparative runs were done (USP 3317628):

TABLE 1.4: The effect of ammonia gas ammoniations.

Catalyst	T(°C)	g prod/g cat	conv(%)
$CoO/NH_{3(g)}$-C	85	20,5	51,3
	25	21,7	51,1
B-$CoO/NH_{3(g)}$-C	85	27,4	70,2
	25	38,2	93,7

Liquid ammonia was also tested. Carbon was added to liquid ammonia which was cooled by a dry ice-acetone mixture. After standing for 1h the ammonia was evaporated by letting the mixture heat to ambient. The catalyst was then dried for 1h under vacuum, following which 13% CoO was loaded and vacuum dried for 64h at 150°C. After cooling, the catalyst was washed with an excess of liquid ammonia and dried for 22,5h. It was then activated for 5h at 275°C at 50mmHg under 68 ml/min of N_2 and the reaction was carried out at 85°C. This catalyst produced 12,7g product/g cat with a conversion of 43,3%. It was difficult to extract meaningful information from this data as excessive heating periods were used (The sites are known to be thermally unstable - see 1.2.2.4).

In another modification, a pre-ammonium hydroxide treated catalyst was activated as usual, then heated to 150°C with ammonia in a bomb autoclave for 10h. The catalyst was dried in a hood for 5h and reactivated as usual. A liquid production of 40,4 g/g cat was achieved at 85°C corresponding to a conversion of 35%. At 30°C, a conversion of 80% was achieved.

1.2.2.2 The Effect of Acid and Base Carbon Pretreatments

Here, the carbon was first washed in the acid and then the base. It was then loaded with cobalt and activated using the standard procedure (Schuck et al., 1967). No reaction conditions were given except for the assurance that all things were equal. There was no post ammoniation:

TABLE 1.5: The effect of acid/base activated carbon pretreatments.

Acid	Base	g prod/ g cat
HNO_3	NH_4OH	13,8
" "	none	3,3
" "	CH_3NH_2	4,6
" "	$(CH_3)_2N$	4,2
" "	t-$BuNH_2$	12,5
" "	LiOH	6,1
" "	NaOH	3,7
" "	Pyridine	8,0
HCl	NH_4OH	11,2
" "	none	6,8

1.2.2.3 The Effect of Nitrogen/Hydrogen Pretreatments

The following set of data (Schultz, 1967, a) illustrated the advantage of this pretreatment (as described in 1.2.1.3):

TABLE 1.6: The effect of H_2/N_2 pretreatments.

catalyst	g prod/g cat	conversion(%)
CoO/C	8,36	22,1
CoO/N_2-H_2-C	14,2	27,3
NH_4OH-CoO/N_2-H_2-C	20,5	?
CoO/NH_4OH-C	13,6	25,9
B-CoO/B-C	17,1	56,6
B-CoO/N_2-H_2-C	20,9	38,7
B-CoO/B,N_2-H_2-C	19,5	37,5
B-CoO/B-acid-C	13,2	45,9
B-CoO/N_2-H_2,B,acid-C	20,7	61,7
B-CoO/B,N_2-H_2,B,acid-C	21,6	73,5

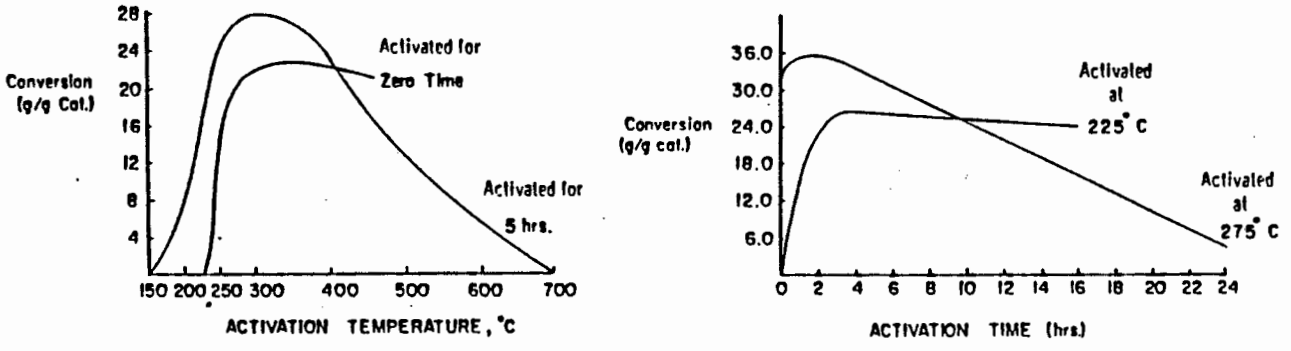
CoO/C	8,0
CoO/B-C	13,0
CoO/N_2-C	13,5
B-CoO/B-C	28,5
B-CoO/N_2-C	32,6

It was apparent that the nitrogen and ammonium hydroxide pretreatments were equivalent. This data was difficult to interpret further because of the similar liquid productions with vastly differing conversions.

1.2.2.4 The Effect of Activation Time and Temperature

The following figures (Fig. 1.1) were reported by Schultz et al. (1966a) showing data for the double ammoniated catalyst:

Fig. 1.1: Batch activities with variable calcination conditions.



These trends were explained in terms of a thermal decomposition of active sites. It was not clear whether this phenomenon was due to sintering, oxidation state change or loss of ammonia. Schultz et al. (1966a) did not find any significant trends in the oxidation state of the cobalt between fresh and spent catalysts. The analytical method used by them to determine the proportions of the various oxidations states was a series of leachings - chlorine, acetic anhydride and finally aqua regia to extract the metal, Co^{2+} and Co^{3+} respectively. The results of such a procedure were questionable. They did not report oxidation state data for varying calcination conditions. It is also possible that the calcining nitrogen contained trace O_2 which could explain the near

linear degradation in activity with exposure to calcining gas. It should be noted that the half cell potential for the reduction of Co^{3+} is strongly influenced by the presence of ammonia (Mahan, 1972):

TABLE 1.7: Standard Cell Potentials.

$Co^{3+} + e^- = Co^{2+}$	E°=+1,8 V.....i
$Co^{3+}(NH_3)_6 + e^- = Co^{2+}(NH_3)_6$	E°=+0,1 V.....ii
$Co^{2+} + 2e^- = Co$	E°=-0,28 V.....iii

It is evident that a loss of ammonia through excessive calcining would significantly affect the ability of any Co^{3+} to resist reduction by poisons or by the propene itself. It is also possible that part of the catalyst activity arises through the ability of the cobalt to switch oxidation states i.e., the forward and reverse reactions of (ii) above. A loss of ammonia would energetically retard such a mechanism as shown by the large increase in E°.

1.2.2.5 The Effect of Sodium and Potassium Promoters

A catalyst containing 18 wt% of metallic cobalt was synthesized by impregnation with a nitrate solution and activated at 300°C in an inert atmosphere. This activated catalyst was treated with 15% (by mass) of sodium or potassium at temperatures above the melting point of the metal. After allowing a batch reaction for 1h, the following set of data was generated (Addy and Hill, 1968, a):

TABLE 1.8: The effect of alkali metal promoters - batch data.

Alkali metal	none	K	K	none	K	Na	none
Reaction T(°C)	80	80	85	87	76	85	72
% C_6 in prod	nd*	84	86	nd	91	88	96
g prod/g cat	1,2	5,8	7,1	2,4	6,1	9,8	1,5

*.... nd = not determined

However, it is questionable whether the alkali metals were simple promoters. Alkali metals are known to dimerise propene. Hambling (1969) carried out the following reactions at 150°C and ca. 100 atm:

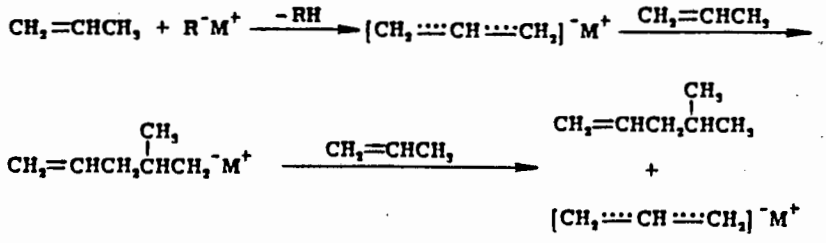
TABLE 1.9: Base catalyzed oligomerization.

Catalyst (wt% alkali)	rate of reaction (gm C_6/gm-atom alkali metal·h)	(g/gcat·h)	selectivity to C_6	Composition of C_6 (%)*
K/graphite(11,9)	120	14,3	98	62:24:4:6:4
K/graphite(5,1)	97	4,9	98	30:50:4:12:4
K/K_2CO_3(4,4)	150	6,6	98	75:16:0:1:8
Na/graphite(3.0)	155	4,7	89	21:56:5:15:3
Na/K_2CO_3(3,7)	91	3,4	98	74:18:0:1:7

* Ratio= 4M1P:4M2P:2M1P:2M2P:n-H

The proposed reaction mechanism (by Pines, 1981) for the high 4-methylpent-1-ene was as follows:

Fig. 1.2: Mechanism for base catalyzed oligomerization.



The above data suggests that the "promoters" could have been active with out the presence of the cobalt. The authors presented no data to suggest that this is not true.

1.2.3 Integral Reactor Run Data

Schultz et al. (1966a) were the only workers to report in detail on their

tubular flow through reactor run data. Their best run with their double ammoniated cobalt on carbon catalyst produced a total of 606,5g of liquid per gram of catalyst. The run lasted 222h and had an overall conversion of 15,5%. The reaction temperature was in the range 36-62°C, the pressure was 50 atm and the average WHSV was 17,6h^{-1}. By comparison, the non-ammoniated equivalent lasted 6h and produced 0,72g/g cat. All other workers who reported integral reactor run data gave only initial rates of liquid product formation. Addy and Hill (1968a) reported productivities of their alkali promoted catalysts in 30 min intervals over 2h. It is deemed unlikely that significant lifetimes were attained. Their run data is shown below:

TABLE 1.10: The effect of alkali promoters.

Run	1	2	3
Temp of sodium treatment (°C)	none	120	175
Productivity (g/g·h)			
0-30 min	1,65	10,8	8,0
31-60 min	1,5	8,0	6,7
61-90 min	-	-	5,0
91-120 min	-	-	6,0

The following data (Addy and Hill, 1968, b) illustrate the bi-metallic system where the second metal added supplied the nitrate ion. Under the conditions of 20 atm, 20°C and a WHSV of 10h^{-1}, the following metals were tested:

TABLE 1.11: Bi-metallic catalysts.

% cobalt:	2%				5%				
nitrate added:	none	Cu	Ni	Cr	none	Cu	Ni	Cr	
Activation conditions:									
temp (°C)	350	350	450	450	350	350	450	350	450
time (h)	4	3	2	2	4	3,5	2	4	1
Activity (g/g·h)	none	0,63	0,63	0,51	none	4,16	1,8	1,5	1,5

It is evident from this data that either the nitrate was in fact necessary or that another metal was necessary. The activity increased markedly as the cobalt content was raised from 2-5 wt%. The effect of increasing the metal loading further was not indicated.

The following run data shows the effect of inert gas treatment on a copper-cobalt catalyst which had had no nitrates present and which had been heated between 200-300°C in a stream of N_2 containing 10% O_2. Run conditions were 20 atm, 20°C and WHSV of $4h^{-1}$:

TABLE 1.12: The effect of activation temperature.

Run	1	2	3	4
Pretreatment temp (°C)	none	350	400	400
Activity (g/g·h)	0,03	0,48	3,1	4,0

The effect of activation temperature was evident. The fairly large disparity between run3 and run4 suggested a possible wide spread in activities for the same catalyst.

The relative merits of the above systems could not be conclusively compared because of the lack of lifetime, conversion or total liquid production data. The double ammoniated catalyst did however appear to be superior.

1.2.4 Typical Product Spectra and Proposed Mechanisms

In spite of the widely varying operating conditions of all the literature data, the distribution of C_6 isomers appears to be consistent throughout. Schultz et al. (1966a) believed that their products were primary reaction products.

TABLE 1.13: Literature product spectra.

Catalyst(*)	1	2	3	4	5
4M1P	2,4	5	4,3	4,0	3,9
c-4M2P	9,9	18,8	15,8	16,6	11,1
t-4M2P	26,7	21,1	18,4	20,0	27,2
2M1P	3,4	2,6	3,1	3,6	3,7
2M2P	2,4	1,4	1,8	trace	2,1
2,3DMB	nd	nd	nd	nd	2,1
1H	1,3	1,8	2,4	0,2	2,0
c-2H	15,1	21,7	23,4	21,4	13,0
t-2H	31.0	25,8	28,7	30,4	28,8
c-3H	1,4	0,5	0,6	1,9	1,9
t-3H	6,3	1,2	1,5	1,9	5,5
% Total Linear	55	nd	56.5	nd	54,2
% C_6 in Product	91	nd	94,6	nd	95

*••• References: 1- Dutch patent 641239; 2- Addy and Hill (1968a) 3- Hill (1969); 4-Addy and Hill (1968b); 5- Schuck et al. (1967)

Schultz et al. (1966a) suggested that their active species was a cobalt hydride L_3Co-H where the ligands (L) were co-ordinated with the activated carbon surface. The hydride ion was believed to have been generated by reaction with ammonia. Some doubt is cast by the data of the other workers who obtained high initial activities and similar spectra (Table 1.13) in the absence of a proton source like ammonia.

After chemisorption of propene, Schultz et al. (1966a) propose an insertion mechanism which parallels that of the homogeneous hydroformylation reaction. The isomer distribution is well predicted by this mechanism. No other workers attempt to explain the mechanism or nature of the active sites on their catalysts.

1.2.5 Two Step Linear Tetramer Synthesis

From the previously discussed literature, it is evident that the cobalt-carbon system has a high tendency to dimerise its feed stock. The question is posed as to whether the catalyst is able to re-dimerise the dimer product to produce tetramers. In their patents, Schultz and co-workers discuss some tests done.

In one experiment (Schuck et al., 1967), the dimer product from a typical double ammoniated catalyst was distilled to give a normal hexene fraction containing: 0,71% t-4M2P; 2,81% 1H; 3,24% 2M1P; 3,36% T-3H; 0,82% C-3H; 55,15% T-2H; 1,10% 2M2P and 32,89% C-2H. This feed was passed over a double ammoniated catalyst which had been activated in N_2 at 475°C for 3h. At a reaction temperature of 150°C, a productivity of 4,46g propene tetramer/gram of catalyst was obtained corresponding to an average conversion of 6,39%. The product was essentually n-dodecene, methylundecene and ethyldecene.

In order to probe the reaction further, pure hexenes were tested as feed stocks. Batch tests showed an 18,6% conversion of 1-hexene at 150°C following a 275°C activation. After hydrogenation, the product contained 82,8% n-dodecane. Higher calcination temperatures (ca. 450°C) reduced conversion to 8,5% and decreased dodecene selectivity to 55,5%. When 2-hexene was fed over the catalyst activated at 275°C , no activity was observed. As activation temperature was further increased (adding isomerising functions), conversion increased to a maximum of 13,3% and productivity of 3,5g product/g catalyst. It was found that the ammoniation procedure in no way promoted this reaction. This result agrees with the product spectrum of the propene dimerization reaction where 1-hexene was obtained as a trace compound compared to the 46% 2-hexene in the dimer product.

The conversion and productivity for a second dimerization step were thus low when using cobalt oxide on activated carbon catalysts. BP workers have patented the process (Dutch Patent 6412392) whereby a dimeric product is produced via a cobalt-carbon catalyst. The dimer is then

redimerized by more durable catalysts e.g., transition metals supported on silica alumina. The product was more linear than that produced by other two step systems. The motivation for a linear product in their work was for the synthesis of a biodegradable detergent. The success of any two step process would clearly depend on the choice of the catalyst for the second step.

1.2.6 Catalyst Regeneration

Schultz and co-workers do not address regeneration in their published work dicussed in the preceding sections. Hill (1966 and 1970) proposed two regeneration methods. The first required the heating of the spent catalyst in a nitrogen stream to remove residual reactants and products (purging with hydrogen was also considered to be effective here). This was followed by a stream of nitrogen containing air and finally flushing with pure nitrogen. In an example quoted, a catalyst containing 5% cobalt and 15% copper was heated from 100-200°C in the gas stream (50ml/min air: 300ml/min N_2) over 3h and held for 2h. The temperature was then increased to 400°C and held for 3h. The catalyst was totally regenerated. Presumably, the temperatures selected were relevant only if the catalyst was capable of withstanding them.

The second proposed method required a pretreatment of the spent catalyst with air in the temperature range 300-450°C until combustion of hydrocarbon deposits was complete. This was followed by a treatment with a stream containing NH_3, O_2 and H_2O in N_2. The ammonia could be added in any convenient way (eg., bubbling the gas stream through ammonia solution). Contact temperatures of 100-120°C were preferred. The temperature had to be such as to avoid the formation of condensate which would leach out the cobalt. Finally, the catalyst had to be flushed with N_2 or treated under vacuum at 300-450°C.

1.2.7 Ethene Oligomerization

In the 1940's, Cheney et al. (1950) developed a cobalt-activated carbon catalyst for ethene oligomerization. This catalyst was produced by

aqueous impregnation of activated carbon with cobalt nitrate. The solvent was removed and the nitrate decomposed by heating to 300°C with agitation. A major problem encountered was the spontaneous combustion which occured during the nitrate decomposition. Localised hot-spots were found to cause non-uniform activity. Cheney patented several methods to overcome this problem (USP 2407813 and 2407814). The simplest was to continuously add solvent whilst the nitrate was decomposing.

The catalyst could be activated either in H_2 for 3-6h at 300°C or by heating in the presence of an inert gas or vacuum. Cheney et al. (1950) reported without detail that the differing procedures gave differing product spectra; the non-reduced catalyst gave lower dimerization selectivity but was more active.

A typical average polymer production rate of 310g/l·h (ca. 0,5g/g·h) over 40h was obtained. Cheney et al. (1950) however, found that propene oligomerization had 1/40 this activity. Schultz (1967) compared his double ammoniated catalyst for ethene oligomerisation with a non-ammoniated catalyst. In a batch reactor experiment, the non-ammoniated catalyst gave a 74,4% conversion at 25°C over 24h compared to the 94,6% conversion of the double ammoniated catalyst under the same conditions.

1.3 ACTIVATED CARBON

In the preceding sections on the cobalt-activated carbon catalyst system, it was evident that this catalyst depends strongly on the nature of the activated carbon support. This section develops the background necessary to elucidate some of the phenomena of the cobalt oxide on carbon catalysts.

1.3.1 Manufacture

Activated carbon is manufactured according to two generalized procedures (Smisek and Cerny, 1970):

i) The first involves the carbonization of carbonaceous materials, eg. coal, coconut and bone at high temperature. These temperatures are typically in the range 400-600°C. In this process most of the non-carbon elements, e.g. hydrogen and oxygen, are driven off and the freed carbon atoms form graphitic crystallites. These crystallites are disorganised and irregular. The surface area of this carbon intermediate is low and consequently its absorptive ability is also low. The intermediate is activated typically by steam, carbon dioxide or oxygen by the following reactions:

$$C + H_2O = CO + H_2 \qquad (750\text{-}950°C)$$
$$C + O_2 = CO \text{ or } CO_2 \qquad (600\text{-}800°C)$$
$$C + CO_2 = CO \qquad (850\text{-}1100°C)$$

Micro-pores become unblocked of tars and, depending on the degree of reaction, the crystallites themselves may be partially reduced in size causing the formation of macro-pores. Surface area increases from $100m^2/g$ to $1000\ m^2/g$ are typical.

ii) The second manufacturing procedure involves the use of an activating agent, typically zinc chloride. The starting material is treated with the activating agent at elevated temperatures. After thorough mixing, the impregnated material is calcined at temperatures in the range 400-1000°C, the optimum temperature is 600-700°C for zinc chloride. The activating agent inhibits the formation of tars and possibly promotes the formation of crystallites. After calcination, the activating agent is leached out of the carbon. It has been found that the volume of leached salts is proportional to the pore volume and hence the control and use of the quantity of starting agent is an important variable. On account of the lower activation temperatures, crystallites are smaller than for the first method, giving greater porosity.

By the very nature of the carbonaceous starting material, the pore sizes of the activated carbon are totally random. In general, the activated carbon cannot provide shape selective adsorption or catalytic reactions. Smisek and Cerny (1970) reported an exceptional case: the activated

carbon manufactured by the thermal decomposition of polyenylidene chloride or a copolymer of vinylidene and vinyl chloride (Saran). By varing the carbonizing temperature, the effective pore diameters can be increased from 6.2 to 12 A. These activated carbons could provide useful shape selectivity in catalytic reactions (such as the production of linear oligomers).

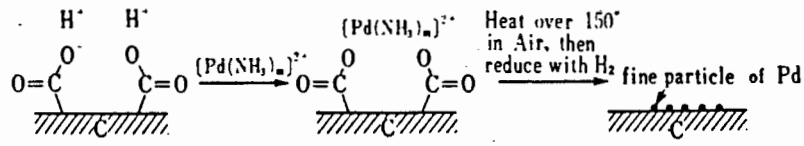
1.3.2 The Surface of Activated Carbon

The surface of activated carbon is extremely complex. The random orientation of the crystallites and the presence of imperfections gives surface carbon atoms of varying valence states and degrees of bonding. Depending on the starting material, ash will also be present on the surface. Oxygen and hydrogen atoms will be present in amounts depending on the starting material and the method of manufacture. According to Kipling (1956), these atoms are essential for good adsorptive properties. Functional groups which have been detected on the surface include carbonyl, carboxyl, phenol, lactone, quinone and etheric groups (Cookson, 1978). It is evident that there are both acidic and basic oxides present on most activated carbon sufaces. The proportion of these oxides depends on the activation procedure. For example, Coughlin (1969) reported that basic oxides predominate after the activated carbon had been heated in vacuo or in an inert gas and allowed to come into contact with air only after cooling. The acidic oxides are produced during normal manufacture procedures.

The presence or absence of oxygen functional groups strongly influences the interaction between activated carbon and aqueous solutions. Firstly, oxygen functional groups (being polar in charge) make the surface hydrophillic. Secondly, the activated carbon is then able to adsorb ionic species. This adsorption could include ion-exchange. Walker and Janov (1968) undertook water adsorption experiments with graphetized carbon. The original carbon had a surface area of 82 m^2/g and had been heated to 2800°C. By partially oxidising the surface in air at 500°C, they observed a marked improvement in the water adsorption. In similar experiments, Healey et al. (1955) found that water was adsorbed not

randomly but in clusters grouped possibly at the edges of graphitic planes. Bartholomew and Boudart (1972) used similar partially oxidised carbon for the synthesis of a well dispersed platinum-iron alloy catalyst. Not only did the partial oxidation improve the uptake of impregnated salts and surface area, but also dispersion was improved. They speculated that new pores prevented metal crystallite growth and crystallite migration during reduction. In addition, Morikawa et al. (1969) proposed that ion-exchange with oxygen functional groups improved the dispersion of their platinum catalyst. The following scheme was proposed:

Fig. 1.3: Ion-exchange of a platinum salt onto activated carbon.



The electronic properties of the surface are also important. Coughlin (1969) reported that the resistivity of crystallites at room temperature in the direction parallel to the planes is of the order of 10^{-4} ohm-cm. The perpendicular resistivity is approximately 1 ohm-cm. The random orientation of crystallites thus offers both conductor and semi-conductor properties. Impurities such as chemisorbed oxygen can withdraw (or provide) electrons and strongly affect the electronic nature of the surface (Walker et al., 1965). Ash on the surface provides insulator properties.

1.3.3 The Catalytic Properties of Activated Carbon

Various authors (Coughlin, 1969 and Bond, 1962) have related catalysts which are conductors, semiconductors and insulators to classes of reactions. For instance, insulators polymerize while conductors hydrogenate. In the previous section, it was observed that activated carbon exhibits all three electronic properties. It is not surprising to find that activated carbon catalyzes reactions from all three classes. A

sample of these systems is discussed below. The emphasis in the following section is on the nature of the active sites.

1.3.3.1 Carbon Catalyzed Formation of Hexaammine Cobalt(III) in Solution

Bjerrum and McReynolds (1946) first reported that decolourizing charcoal catalyzed the synthesis of hexaammine cobalt(III) salts. The reaction was:

$$4\ Co(NO_3)_2 + 4NH_4NO_3 + 20NH_3 + O_2 = 4[Co(NH_3)_6](NO_3)_3 + 2H_2O$$

where the oxygen was supplied by an air sparger. Typically 4h was necessary for completion of the reaction at room temperature. The authors report in a footnote that charcoal taken "from the centre of a package has been found to be much more effective than that from the top." This suggests an inhibition due to air oxidation.

Mureinik (1977) analysed the kinetics of the similar system of the carbon catalysed conversion of $[Co(NH_3)_5(OH)]^{2+}$ to $[Co(NH_3)_6]^{3+}$. The reaction

$$[Co(NH_3)_5(OH)]^{2+} + NH_4^+ = [Co(NH_3)_6]^{3+} + H_2O$$

had

$$K_{eq} = \frac{[Co(NH_3)_6^{3+}]}{[NH_4^+][Co(NH_3)_5(OH)^{2+}]} = 25 \pm 7\ M^{-1}.$$

On the basis of his kinetic data, Mureinik proposed an eight step reaction mechanism which required the presence of basic sites. Factors supporting the existence of basic sites on the charcoal used (Decolorising Charcoal C177, Nucher C190N of Fischer Scientific Co.) were:

i) the addition of charcoal to water caused the pH to increase by 0.3.

ii) degassing of the charcoal liberated "considerable quantities" of carbon dioxide. Possible basic sites could therefore have been carbonates formed by the adsorbed CO_2;
iii) the addition of small quantities of Na_2CO_3 enhanced the reaction rate by 10-15%.

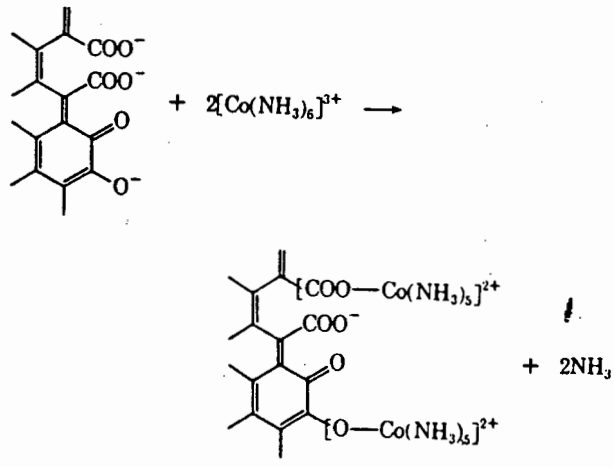
Mureinik also found that the addition of Co(II) ions caused a marked catalytic improvement. Analysis of the initial reaction system showed no detectable Co(II). Dwyer and Sargeson (1960) suggested that activated carbon behaves as an electron sink for the repeated switching of cobalt ions between the II and the III valence states. They believed that the Co(II) is the active state.

Tomita and Tamai (1971) studied the reverse reaction, ie.,

$$Co(NH_3)_6^{3+} + H_2O = Co(NH_3)_5(OH)^{2+} + NH_4^+.$$

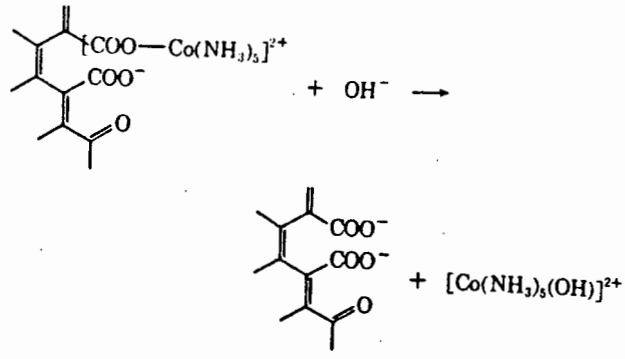
The objective of their work was to investigate the relationship between surface acidity and the rate of hexaammine adsorption and the dependence of the catalytic activity on the surface acidity. Samples of carbon black and activated carbon were modified by treatments with HNO_3, $(NH_4)_2S_2O_2$, O_2 (oxidations) and CH_2N_2 (methylation). The methylation affects the surface carboxyl or hydroxyl groups. The degree of ensuing acidity was measured by simple sodium hydroxide consumption measurements. The rate of adsorption of the hexaammine was found to be directly related to surface acidity. Tomita and Tamai (1971) proposed the adsorption mechanism showm in Fig. 1.4. This was supported by the following three facts:
1) adsorption was promoted at high pH where -COOH functional groups would be converted to $-COO^-$;
2) at low pH the converse occurred;
3) methylation reduced the rate of adsorption.

Fig. 1.4: Adsorption of cobalt complex onto activated carbon.



The hydroxylpenta-amine was then formed from these adsorbed species:

Fig. 1.5: Desorption of hydroxypenta-amine complex.



They also observed the formation of multilayers which they could not characterise on the information available.

1.3.3.2 The Racemization of 1,1-Binaphthyl by Carbon Surfaces

Solutions of optically active binaphthyl are racemized naturally with a half life of 12h (Coulter and Clemens, 1964). The addition of small amounts of active carbons completely racemizes the solution in minutes. Pincock et al. (1976) undertook kinetic studies of this reaction in the hope of revealing the catalytic nature of the carbon. They made three

mechanistic proposals, none of which were conclusive but they do explain some phenomena. The first was that the aromatic rings were adsorbed in planar fashion onto the planar crystallites to form the transition state for racemization. This is supported by the fact that larger aromatics (eg. anthracene or perylene) inhibited the reaction and the use of benzene as a solvent totally inhibited the reaction. Secondly, they proposed that various functional groups on the edges of the planar surfaces bonded loosely to the binaphthyl by electrophilic attack. This would improve the stability of the transition state and aid rotation. This theory was supported by the fact that degassing the carbon for 16h at 100°C in vacuo halved the catalytic rate. Thirdly, they proposed that reversible electron transfer to the binaphthyl from the carbon took place. This would result in greater reasonance stability.

Pincock et al. (1976) also found that the acidity/basicity of the carbon was not an important factor and that the presence of water or ethanol had no effect. These factors eliminated any other reaction mechanisms.

1.3.3.3 Carbon Black Catalyzed Olefin Isomerization

Meier and Hill (1974) investigated the isomerization of 2-methyl-1-pentene to 2-methyl-2-pentene over carbon black (Black Pearls 2 from Carbot Corp). The temperature range investigated was 0-52°C. The proposed mechanism was simply:

Fig. 1.6: Mechanism of olefin isomerization.

$$CH_2{=}CCH_3CH_2CH_3 + R\text{-}D = CH_2DC^+CH_3CH_2CH_3 + R^{-1} = CH_2DCCH_3{=}CHCH_3 + R\text{-}H$$

shown here with deuterium exchanged Bronsted acid sites. The acidic hydrogen content of the carbon black was 1.3 meq/g. The carbon was catalytically inactive when in equilibrium with atmospheric moisture. From this and controlled wetting it was concluded by the authors that there was a range of active sites and that the most active ones were preferentially poisoned by water. By using the deuterium exchanged carbon black it was found that only a few sites were involved in the

reaction. For example, after the formation of 3,1 mmoles of 2-methyl-2-pentene by a catalyst containing 1,73 meq of deuterium, 80% of the deuterium still remained on the carbon. At lower temperatures even less deuterium was lost. The standard pretreatment for the carbon black was a degassing at 160-165°C for 20h at a final pressure of no less than 10^{-6} torr.

1.3.3.4 Other Systems Catalyzed by Carbon

A list of systems of interest is given below. Any relevant information on the nature of sites and the reaction are inclured:

i) Desulphurization : $2H_2S + O_2 = 2H_2O + S$ (Smisek and Cerny, 1970).
ii) Phosgene synthesis (Smisek and Cerny, 1970).
iii) Decomposition of hypochlorous acid (Smisek and Cerney, 1970).
iv) Synthesis of HBr.
Coughlin (1969) reviews this reaction. The proposed mechanism is that of an "acceptor" reaction ie., it has an adsorbed bromide intermediate. The formation of this intermediate depends on the presence of transferable electrons. Comparisons between the activity of graphite and metal chloride-graphite intercalation (or lamellar) compounds support this requirement. The chlorides act as electron acceptors and the HBr synthesis is decellerated. Further, the liberation of electron withdrawing oxygen functional groups improves synthesis rates.
v) Dehydrogenation of formic acid (typical of a conductor) and 2-propanol (Coughlin,1969).
vi) Oxidation of H_2O_2 and SO_2:
The proposed mechanism (reviewed by Coughlin, 1969) is as follows:

$$C^+]OH^- + H^+OOH^- = C^+]OOH^- + H_2O$$

$$C^+]OOH^- + H_2O_2 = C^+ + H_2O + O_2$$

where $C^+]$ represents the activated carbon surface.
The oxidation is favoured by a catalyst pretreatment with oxygen.
vii) Polymerization of liquid α-olefins over carbon blacks (Coughlin, 1969).

viii) Coughlin (1969) observed that the lack of evidence for cracking activity is probably due to the loss of oxygen functional groups at the elevated temperatures necessary for cracking.

1.4 Supported Cobalt Catalysts: Cobalt on Aluminosilicates

The aluminosilicates are an extremely important group of catalysts. Not only are they acid catalysts but they also serve as good supports for metallic catalysts. Important generalised features of aluminosilicates include thermal stability; modifiable acidity and an ability to undergo ion-exchange. The classes which fall into this group include pure alumina, silica, amorphous silica alumina, clays and the zeolites. The zeolites have the added feature of offering increased selectivity through steric hindrance.

These aluminosilicates form an excellent group to counter-foil the properties of the activated carbon support discussed previously. Catalysts synthesized from cobalt supported on these aluminosilicates will be able to test the need for a cobalt-carbon interaction, the need for Co_3O_4 crystallites, the need for an acidic or neutral support and finally the need for steric effects. Further, by testing each catalyst in its own right, a new propene oligomization catalyst could be discovered.

The ensuing sections set out to outline the behaviour of typical members of the above classes of aluminosilicates and then to report the literature on cobalt modified versions. Relevant reaction systems and catalyst characterisation will be discussed.

1.4.1 Cobalt on τ-Alumina

Cobalt supported on τ-alumina has found widespread application in the industrially important reactions of hydrocracking, hydrogenation, hydrodesulphurizaton (HDS), methylation and synthetic fuel synthesis. Generally, where cobalt is associated with τ-alumina, it it serves as a

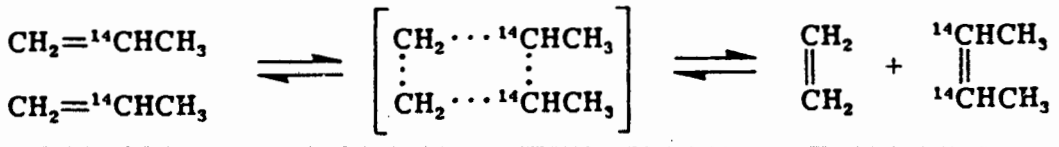
promoter with other metals such as molybdenum and tungsten. The interaction between these metals and the support have been the subject of much research (Topsoe and Topsoe, 1982; Burggraph and Leyden, 1982; Gil-Llambias and Escudey-Castro, 1983; Arnoldy and Moulijn, 1985). In order to gain an understanding of these systems, work has been done on characterising the cobalt γ-alumina catalyst.

The catalyst is generally made by nitrate impregnation and thermal decomposition. The literature is in agreement that there are two basic phases present in the system: a crystalline B-phase and a dispersed D-phase. The D-phase occurs for CoO loadings greater than 2%. The D-phase consists of Co^{2+} ions dispersed through surface layers of the alumina. This phase is often referred to as $CoAl_2O_4$. It is found to be nonreducible and nonsulphidable. The B-phase consists of Co_3O_4 crystallites which are easily reduced and sulphided. The Co^{3+} was found only in these crystallites.

Arnoldy and Moulijn (1985) have used the technique of temperature programmed reduction coupled with XRD to investigate the phase changes which cobalt γ-alumina undergoes in the presence of H_2. They have identified at least eight subspecies of those discussed above. Of relevance are their findings that i) the presence of NO_2 (formed during calcination of the nitrate) affected the valency of the cobalt and consequently the dispersion; Co^{2+} ions dispersed well while Co^{3+} ions tended to sinter forming Co_3O_4 crystallites; ii) the tendency of Co^{2+} ions to diffuse into the alumina increased with increasing calcination temperature (which, in the case of HDS, results in a loss of activity).

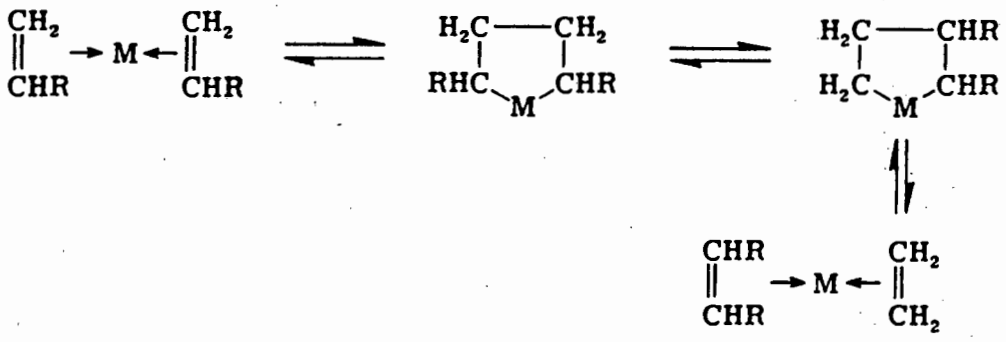
Cobalt has been closely associated with the metathesis reaction. For example, Pines (1981) reported that a good catalyst for propene metathesis at 205°C consisted of 3,4% Co, 11,0% MoO_3 and 85,6% Al_2O_3. The role of the cobalt was seen to be that of a promoter. The reaction was thought to precede via a cyclobutane intermediate:

Fig. 1.7: Mechanism of metathesis reaction.



An objection to this mechanism is that it does not account for the nature of the metal and hence the following was proposed :

Fig. 1.8: Modified mechanism of metathesis reaction.



The classic work on the metathesis of propene over Co/Mo-γ-alumina catalyst was done by Banks and Bailey (1964). At 160°C and 30 atm at a WHSV of 14,5h^{-1} with a 60/40 propene propane feed and a run time of 2h, a conversion of 37,2% was obtained. The theoretical maximum conversion is 42,3% at 25°C or 47,8% at 540°C (Mol and Moulijn, 1975). Their product distribution was 32,4% ethene, 1,7% n-butene, 36,9% t-but-2-ene, 20,2% c-but-2-ene and 8% residue.

Adams and Brandenberger (1969) investigated heavier reactants. They found the following distributions of primary products:

TABLE 1.14: Primary olefin metathesis products

Feed olefin	Product olefins
1-Pentene	Ethylene
	n-Octenes
2-Pentene	2-Butene (43.6 mol%)
	n-Hexenes (44 mol%)
1-Pentene/2-Pentene	Propene
	n-Heptenes
	1-Butene
	n-Hexenes
1-Pentene/1-Hexene	Ethene (36 mol%)
	n-Nonenes (31 mol%)

With increasing molecular weight and mixed feed, selectivity to single products was reduced.

1.4.2 Cobalt on Silica Alumina

Silica alumina is well known in the petroleum industry as the first important hydrocarbon cracking catalyst. It is an amorphous polymeric type of structure where acidity has arisen through the occasional isomorphic substitutions of aluminium for silica atoms. n-Butylamine titration reveals ca. 0,55mmol of acid sites per gram (Pines, 1981). The acidity is a function of the silica to alumina ratio and maximum acidity occurs for a weight ratio of ca. 9:1. Pore sizes are generally large (15,7± 9,6A) and surface areas of 540m^2/g are typical (Ramser and Hill, 1958).

Nickel supported on silica alumina has long been known to be an effective oligomerizing catalyst. Hogan et al. (1955) reacted a cracked gas (containing ethene, propene and butene) at 65-75°C and 34 atm over a 4 wt% Ni on silica alumina (10 wt% alumina). After 100h on stream, the conversion dropped from 99% to 96%. Various workers (Fel'dbyum and Baranova, 1971; Hogan et al., 1955 and Takahashi et al., 1969) have

found that, under the similar conditions to the above, propene diluted with propane was oligomerized to give predominantly dimer and trimer products (but that product spectrum was a strong function of operating conditions). Clark (1953) reported that various transition metals exhibit polymerisation tendencies when supported on silica alumina. Cobalt was catagorised in the same catagory as nickel. This result was contradicted by Eidus et al. (1960) who reported that both cobalt and iron suppressed the activity of silica alumina whilst nickel promoted it. These results were obtained under the conditions of 270°C and atmospheric pressure.

In the synthesis of a nickel silica alumina catalyst, care must be taken to ensure good dispersion, Various workers (Richardson and Dubus, 1978; van Dillen et al., 1976 and Harms, 1987) have found that best dispersion was obtained when nickel hydroxide was precipitated by the slow decomposition of urea. Harms (1987) concluded from propene oligomerization that hydroxide decomposition deposition (HDD) gave the highest activities and lifetimes.

1.4.3 Cobalt on Synthetic Mica Montmorillonite

Synthetic Mica Montmorillinite (SMM) is a good example of the clay catagory of aluminosilicates. It is a 2:1 layered aluminium silicate. Its acidity is in the form of both Bronsted and Lewis sites. Wright et al. (1972) reported that the total acid of calcined NH_4^+-SMM is 4 meq per 100g. Fletcher (1984) found that Bronsted acidity diminished to zero on calcination to 500°C. SMM has a typical surface area of ca. 100m^2/g (Jacobs, 1987).

SMM is known to be active for the oligomerization of propene. Jacobs (1987) reported the following data for a temperature stepping sequence at 50 atm where the temperature was held for 4-6h at each temperature:

TABLE 1.15: Activity vs. temperature for SMM.

Temperature (°C)	Average Activity (g/g·h)
90	0
130	1,9
190	2,3

Notably, SMM had no activity in liquid phase operation.

In a lifetime study of SMM, Jacobs (1987) found an initial induction period of ca. 25h at 50 atm, 130°C and a WHSV of $8h^{-1}$, the activity rose from an initial value of 0,85 to 1,9g/g·h. This induction period was eliminated when 0,05 wt% Co was ion-exchanged into the SMM although lifetime was reduced. No data was available as to whether the cobalt introduced activity in the low temperature liquid phase reaction conditions. Both 1% and 9,5 wt% Ni ion-exchanged SMM had activities of 2,3 and 2,1g/g·h under the above conditions at 90°C. Both Jacobs (1987) and Fletcher (1984) reported that water in the feed (ca. 120vpm) reduced lifetime markedly.

1.4.4 Co(II)Na-Y Zeolites

Zeolite Y was selected as a representative 3-dimensional zeolite for acting as a support for cobalt ions. NaY and its exchanged forms with many cations have been well characterised. Cobalt may be loaded onto the zeolite by impregnation or ion-exchange. The latter had the merits of giving good cobalt dispersion and maintaining the oxidation state of the cation in the state in which it was originally exchanged. Further, the exact siting of the cations relative to the network could be postulated (Yoshida et al., 1974). The protonated form of zeolite Y was also known to oligomerize low chain length olefins to liquid fuels (Fasol, 1983).

1.4.4.1 Synthesis of Co(II)NaY

Two routes were available for synthesizing this catalyst. The first was a direct ion exchange between a cobalt solution and the sodium cations in the zeolite. The second required a pre-ion-exchange with ammonium ions followed by a partial cobalt ion-exchange. The latter method had the merit of introducing controlled amounts of acidity (the ammonium ions decompose upon calcination to give Bronsted sites). All of the literature discussed here used the first method.

Typically, the zeolites used were synthesized by Union Carbide (Linde, SK40). Silica to alumina ratios varied from 4,6 (Tsuruya et al., 1980) to 4,9 (Ward, 1971) and 5,05 (Dzwigaj et al., 1983). Tsuruya et al. (1980) pretreated their NaY with a 2 week impregnation with 1M sodium acetate. No other pretreatments were suggested. The cobalt was exchanged from solutions of the nitrate, sulphate or chloride. For high percentage exchanges, repeated exchanges were done at elevated temperatures (90-100°C). A partial exchange of 70% could be achieved in three exchange cycles at ambient temperatures. After ion-exchange, the catalysts were washed in deionised water and dried typically at 120°C. Tsuruya et al. (1980) confirmed that the crystal structure remained un-altered.

1.4.4.2 Co(II)NaY Structure

Yoshida et al. (1974) confirmed the work of Egerton et al. (1972), who reported that Co(II) occupies an octahedral field in the hydrated state and a tetrahedral field in the dehydrated state. The ligands forming the octahedral field were water molecules. The tetrahedral field was believed to be due to three oxygen bonds from the aluminosilicate framework and the fourth an hydroxyl group from residual water. The latter was considered to be present even when evacuated at 400°C. On the basis of diffuse reflectance spectra, magnetic susceptibility data, infrared data and acidity determination, Yoshida et al. (1974) concluded that the cobalt cation was located on the hexagonal ring inside the sodalite units.

1.4.4.3 The Interaction of Co(II)NaY with Pyridine and Other Bases

Infrared studies (ir.) of the catalyst showed the existence of acidic hydroxyl groups on a catalyst calcined at 480°C and 10^{-3} Torr for 16h (Ward, 1971). These were explained by the reaction:

$$M^{2+} + H_2O = MOH^+ + H^+.$$

After pyridine chemisorption, Dzwigaj et al. (1983) observed two types of Bronsted sites. More importantly,they observed a very stong ir doublet at 1448 and 1457 cm^{-1}. The 1448 cm^{-1} band disappeared after outgassing whereas the 1457 cm^{-1} remained even after heating at 350°C. This doublet was interpreted as originating from pyridine adsorbed on sodium and Co(II) ions. The bands at 1448 cm^{-1} and 1457 cm^{-1} represented the bond with sodium and the much stronger bond with Co(11) ions, respctively. Water adsorbed at 200°C was found to displace the pyridine adsorbed on the cobalt.

Tsuruya et al. (1980) examined the oxidation of benzyl alcohol over Co(II)NaY. Of particular interest was their investigation of the promotion of the reaction by the addition of amines. For instance, the addition of piperidine to the alcohol feed (4%) trebled the yield. One percent pyridine addition doubled the yield. The workers believed that Co(II) amine complexes were formed. Howe and Lunsford (1975a and b) reported the existence of such complexes. Support for the existence of these complexes at the harsh calcination conditions were supplied by the ir work discussed above. Tsuruya et al. (1980) also referred to work done on Cu(II)NaY in which the copper cations migrated from the sodalite cages to supercages when ammonia was adsorbed. The resultant species was $[Cu(NH_3)_4]^{2+}$.

1.4.4.4 Some Systems Catalyzed by Co(II)NaY

Yoshida et al. (1974) used the isomerization of 1-butene as a probe reaction in their research on the location of cobalt ions in the CoY lattice. The catalyst was evacuated at 400°C for 3h. At 100°C, the activity of the catalyst was directly proportional to the percentage of cobalt exchanged. They also found that incomplete dehydration (at 250°C as opposed to 400°C) gave higher activities by six to seven-fold

Tsuruya et al. (1980) have also reported the highly selective oxidation of benzyl alcohol to benzaldehyde. The catalyst was pretreated with a mixed oxygen and nitrogen stream at 400°C for 2h. Activity increased monotonically with increasing cobalt content up to 80% exchange. Calcination temperature was optimal for benzaldehyde conversion at 400°C. The promotion of the reaction by amines is discussed above.

Ward (1971) reported that Co(II)NaY also catalyzed o-xylene isomerization, methylcyclopentene cracking and toluene disproportionation. The cobalt catalyst did not rate well compared to other exchanged metals (eg. Ni and Cu).

1.4.5 Cobalt on H-ZSM-5

ZSM-5 is a relatively new zeolite in the literature. Like NaY, it is a three dimensional zeolite but containing pores of smaller diameter (ca.5,5). Protonated ZSM-5 is known to convert alcohols into high octane gasolines (Chang and Silvestri, 1977) and to oligomerize propene (Occeli et al., 1985; Wilshier et al., 1987). It has also been investigated as a potential F.T. catalyst (Stencel et al., 1983).

Stencel et al. (1983) have attempted to identify the cobalt species present in Co/ZSM-5 catalysts. Using incipient wetness impregnation techniques, they synthesized catalysts having 5,1 to 9,5 wt% Co using $Co(NO_3)_2$ and NH_4^+-ZSM-5. A sample was then thoroughly washed and found by AA to have 1,4 wt% Co. The silicon/aluminium ratio was 11. Using X-ray photoelectron spectroscopy, pyridine infrared spectroscopy and knowledge of the unit cell, the following conclusions were drawn:

i) in the high cobalt loading catalysts (5,1; 7,3 and 9,5 wt%), large external crystallites occurred. These crystallites were reducible and active for synthesis gas conversion.

ii) the 1,4wt % catalyst had predominantly ion-exchanged Co^{2+} ions; this corresponded to a 35% exchange. These ions were not reducible and were not active for F.T. conversion. The number of Bronsted sites had significantly been diminished (the intensity ratio of Bronsted to Lewis sites dropped from 1,74 to 0,2).

When impregnating Na-ZSM-5 (Si/Al = 60) with 4 wt % cobalt, Peuckert and Kinden (1984) also obtained a 32% non-reducible cobalt content (ie., ca.1,5 wt%). Using cobalt carbonyl, Dhere and De Angelis (1985) found that smaller crystallites could be made and that the reductive properties of these crystallites were different to those synthesized by aqueous impregnation.

Occeli et al. (1985) reacted 3:1 propene propane over H-ZSM-5 with silica/alumina = 77,5 at a pressure of 47,6 atm and a WHSV of $1,0h^{-1}$. They obtained the following activity data as a function of reaction temperature:

Table 1.16: Activity vs. temperature for NH_4^+-ZSM-5 with Si/Al=77,5.

Temperature (°C)	Conversion (wt%)
204	negligible
260	10,9
315	64,4
371	98,4
399	95,4

In more recent work, Wilshier et al. (1987) undertook propene oligomerization experiments at ca. 24 atm. Their control catalyst had an aluminium content of 1,22 wt% and was synthesized according to Argauer and Landolt (1972). At 190°C a conversion of 90 wt% was obtained. This value remained unchanged when the temperature was raised to 280°C. This work featured excellent liquid analysis. All product was hydrogenated to reduce the number of alkene isomers. From this analysis, it was clear that at 190°C little shape selectivity was present. Wilshier et al. (1987) concluded from this and surface poisoning experiments that the pores were largely blocked by product. At higher reaction temperatures of 280°C, a more selective product was obtained. The single branched

trimer content rose from 3 to 29% of the total trimer content. The product spectrum showed an increased spread in carbon number with temperature. This was attributed to increased cracking.

1.5 Pure Cobalt Oxide Catalysts

Pure cobalt oxide (Co_3O_4) is known to be an effective catalyst for the total oxidation of carbon monoxide, methane and other hydrocarbons. The synthesis work of Pope et al. (1977) and the determination of active sites by Fukushima and Ozaki (1976) and Miyamoto et al. (1984) are discussed below.

1.5.1 Unsupported High Area Co_3O_4 Catalysts

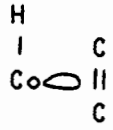
Typical laboratory Co_3O_4 (prepared by thermal decomposition of $Co(NO_3)_2$ at 400°C) has suface areas of a few square meters. Pope et al. (1977) found that surface area was a strong function of starting material and decomposition temperature. For example, $Co(NO_3)_2$ decomposed at 150°C gave a surface area of 50 m^2/g compared to 32 m^2/g for a sample decomposed at 250°C. The conversion to Co_3O_4 was confirmed by x-ray diffraction. As a result of their research Pope et al. (1977) proposed a standard method for high surface area Co_3O_4 via cobalt carbonate decomposition. This catalyst had a typical surface area of 144 m^2/g with crystallite sizes of 70 A and pores of between 20-50 A. Of all starting salts tested for carbon monoxide oxidation, the carbonate precursor was the most active. (At 40°C, ca. 80% CO was removed from a gas stream containing 50 ppm CO at a space velocity of 300000h^{-1}). They noted that the activity of these catalysts was not proportional to surface area. They concluded that Co_3O_4 synthesized from the carbonate had the highest intrinsic activity.

Attempts to prepare pellets of Co_3O_4 were largely unsuccessful. Pope et al. (1977) found that pellets formed from decomposed Co_2CO_3 pellets were stronger than compressed Co_3O_4 powder but lacked viable mechanical strength.

1.5.2 Nature of Active Sites for Isomerization

Fukushima and Ozaki (1976) attempted to investigate the nature of active sites on cobalt oxide with ethene and butene probe reactions and H_2-D_2 equilibration. They found that H_2 could be chemisorbed on Co_3O_4 and that this treated catalyst was extremely active for cis-butene isomerization to trans-butene. They found that the adsorbed hydrogen was rapidly consumed and the catalyst deactivated. Re-adsorption of hydrogen re-activated the catalyst. It was concluded that the active sites for butene isomerization and C_2H_2-C_2D_2 exchange matched Siegels BH model ie., the active site was a cobalt ion to which both an hydride anion and an olefin molecule simultaneously co-ordinate:

Fig. 1.9: Metal hydride active site.



1.5.3 Determination of Active Oxygen Atoms on Co_3O_4 Catalysts

Miyamoto et al. (1984) used the following reaction scheme to determine the number of active oxygens (O_s) on Co_3O_4:

$$2NH_3 + 3O_s = N_2 + 3H_2O \qquad (530\text{-}630K)$$

$$2NH_3 + 4O_s = N_2O + 3H_2O$$

The O_s atoms were suggested as being responsible for catalyzing the oxidation of CO, NH_3 and hydrocarbons. It was concluded that, on average, 3-4 surface Co ions provide a site for an O_s. This result was obviously depended on the synthesis procedure and choice of cobalt starting material.

1.7 Research Objectives

This work set out to investigate various cobalt catalysts as potential propene oligomerization catalysts. The work was split into two major avenues of research. The first involved the cobalt-carbon catalysts. Here the aims were four-fold:

* reproduce the results reported by Schultz et al. (1966,a);
* gain an understanding of the wide ranging activation procedures reported in the literature;
* modify the activated carbon to observe the role of surface functional groups;
* elucidate the nature of the active site by synthesizing and supporting a cobalt hexaammine complex on the activated carbon.

The second avenue involved supporting cobalt on several aluminosilicates. The objectives here were to determine whether:

* cobalt supported on an inert carrier was active;
* cobalt impregnated or ion-exchanged onto acidic supports gave activity at temperatures lower than those typically used for acid catalysts, or modified the selectivity of the acid catalyzed reactions of the raw support.

2 EXPERIMENTAL

The objectives of this chapter are three-fold: firstly, to describe in detail the chemicals and procedures used to synthesize the various cobalt catalysts investigated; secondly, to describe the reactor system and its operation, outlining both the advantages and disadvantages; and finally to discuss the analytical procedures used to characterise the catalysts and reaction products.

2.1 Catalyst Synthesis

2.1.1 Double Ammoniated Cobalt on Activated Carbon

The carbon supported catalyst was modelled on the double ammoniated version proposed by Schultz et al. (1966, a). 33g of a coal based activated carbon (Kopcarb WCM106; particle size = 0,5-1,0mm; surface area = 1150m^2/g; ash content = 2,44%) was soaked with 30ml of 25% ammonia solution (AECI). It was then dried by heating at 130°C. During the drying, the temperature twice reaching 150°C for several minutes. 20,22g of $Co(NO_3)_2 \cdot 6H_2O$ (Carlo Erba) was disolved in 30ml distilled water and added to the carbon. The salt solution brought the carbon to a state of incipient wetness. The wet carbon was dried for 2h on a hot plate until visibly dry and then dried for 18h at 125°C in a vacuum oven (at 1mmHg). After cooling, the catalyst was again soaked with 50ml of ammonia solution, dried on a hot plate and finally vacuum dried (125°C for 26h at 1mmHg). The catalyst was then ready for calcination.

Several modifications were made to the above method. These included varying the duration of post-ammoniation contact and the temperature at which the ammonia was driven off after ammonia treatments. To avoid repetition, these modifications are described in conjunction with the results in section 3.1.

Modifications to the activated carbon starting material were also undertaken:

i) 20g of activated carbon was packed into a reactor in a furnace and heated to 430°C in a stream of pure oxygen flowing at a rate of 150ml/min. The treatment was held for 4h with occasional agitation of the bed to ensure the exposure of all the granules to the stream. The activated carbonn was allowed to cool slowly overnight in flowing oxygen. A 3 wt% mass loss was experienced.

ii) 21g of activated carbon was treated with nitric acid by by the addition of 50ml conc HNO_3 and 50ml distilled water. The mixture was stirred for 20min during which time brown fumes were liberated. The carbon was washed three times with 200ml distilled water. A second batch was treated more severely - 13g of activated carbon was oxidised with 50ml conc. HNO_3 for ½h; the liquor was then decanted and a further 50ml was added. The activated carbon was washed until the pH of the washings was 4. The activated carbon was finally dried at 110°C.

iii) A 10g batch of activated carbon was twice treated with 25ml of 48% HF, the first treatment for 6h and the second overnight. Again, the carbon was washed until the pH of the washings was 4.

2.1.2 Cobalt(III) Hexaammine Supported on Activated Carbon

The cobalt hexaammine nitrate was synthesized according to the method of Bjerrum and McReynolds (1946). In the actual synthesis, 73g $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 100ml distilled water. To this was added 80g NH_4NO_3 and 2g powdered activated charcoal to act as catalyst. Finally, 180ml of conc. NH_3 solution was added. The solution turned rapidly brown with crystals forming. It was allowed to react for 4h with stirring. The reaction took place in a glass vessel exposed to the atmosphere. The solution was filtered. The crystals (still containing the carbon catalyst) were dissolved by warming in 1,3l distilled water and 100ml conc. HNO_3. The activated charcoal was filtered off the hot liquor. Cooling caused precipitation of the now pure orange crystals. These were filtered and washed successively with 100ml distilled water and 20ml ethanol. This washing was excessive and caused a drop in yield.

After drying at 100°C, a yield of 46g of orange-yellow crystals was obtained. Ultraviolet spectral analysis of a solution of these crystals gave the characteristic peak of $Co(NH_3)_6(NO_3)_3$ at 473nm (Mureinik,1977).

Since the complex was only moderately soluble, a loading procedure to support the complex on the activated carbon had to be devised. 6g $Co(NH_3)_6(NO_3)_3.6H_2O$ was dissolved in 600ml distilled water at 60°C. To this solution was added 9g of activated carbon (WCM106). The slurry was stirred via an impellar at ca. 100rpm and the temperature was maintained using a waterbath. Initially, detectable quantities of ammonia were liberated. At various intervals, the carbon was allowed to settle and samples of supernatant liquor were drawn and analysed by U.V. The intensity of absorbance had been calibrated (Fig. 2.1) and hence a direct measure of the quantity of complex loaded could be deduced. A loading curve was generated (see Fig. 2.2). Since evaporation was significant at 60°C, the U.V. data under-read the quantity of complex loaded. Only the final value could be corrected for evaporation once the total volume of liquid had been measured. 4,2g of the complex was loaded and this corresponded to a CoO loading of 9,1%.

2.1.3 Cobalt-τ Alumina

This catalyst was prepared by incipient wetness impregnation. 0,4079g $Co(NO_3)\cdot 6H_2O$ was dissolved in 17ml distilled water and added to 20,2554g τ-alumina. The quantity of water had been pre-determined to be just sufficient to wet all the alumina without an excess of liquid. The catalyst was dried at 107°C overnight to give a 10 wt% Co catalyst.

2.1.4 Cobalt-Silica Alumina

A method well known in the synthesis of nickel silica catalysts is that of homogeneous deposition-precipitation in the presence of urea (Richardson and Dubus, 1978). On account of the close analogue between nickel and cobalt, this method was applied in the synthesis of the cobalt silica alumina catalyst.

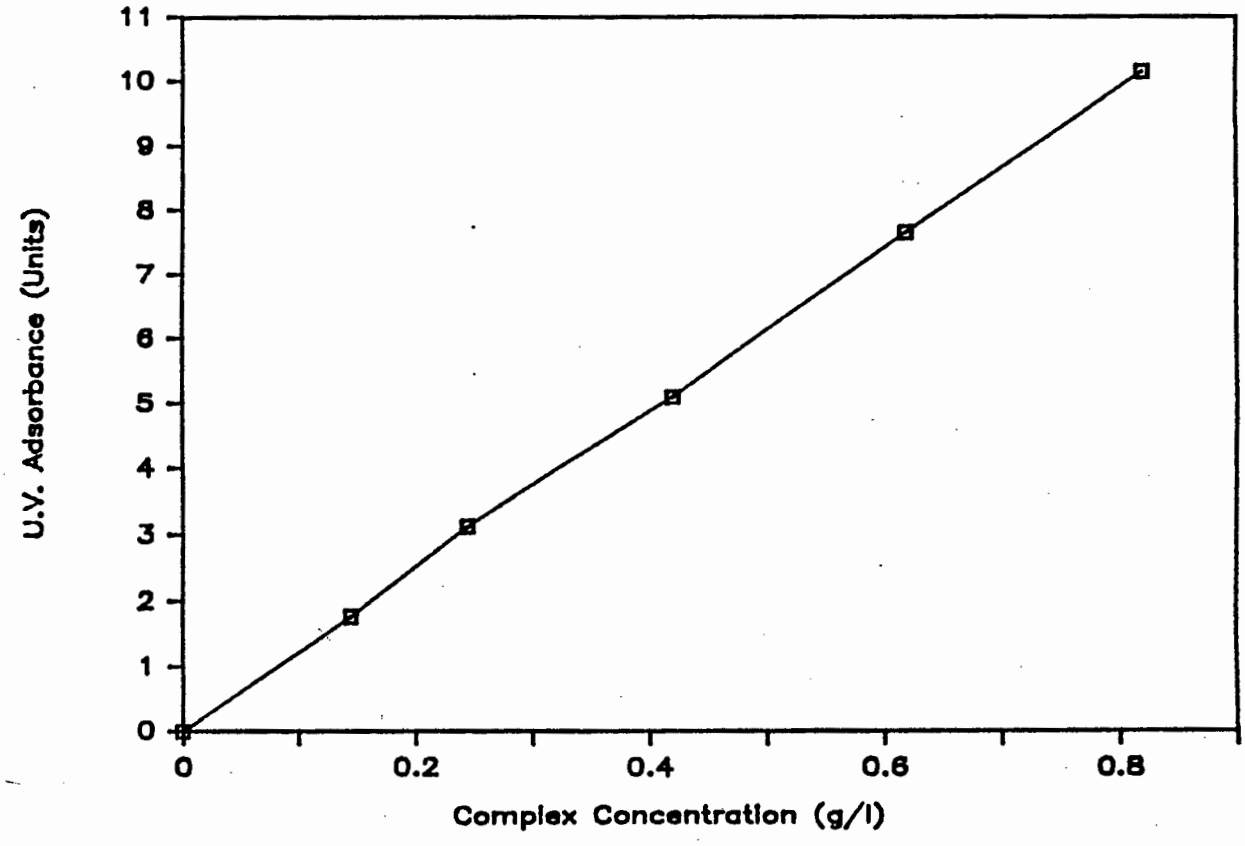


Fig. 2.1: U.V. calibration curve for complex solution.

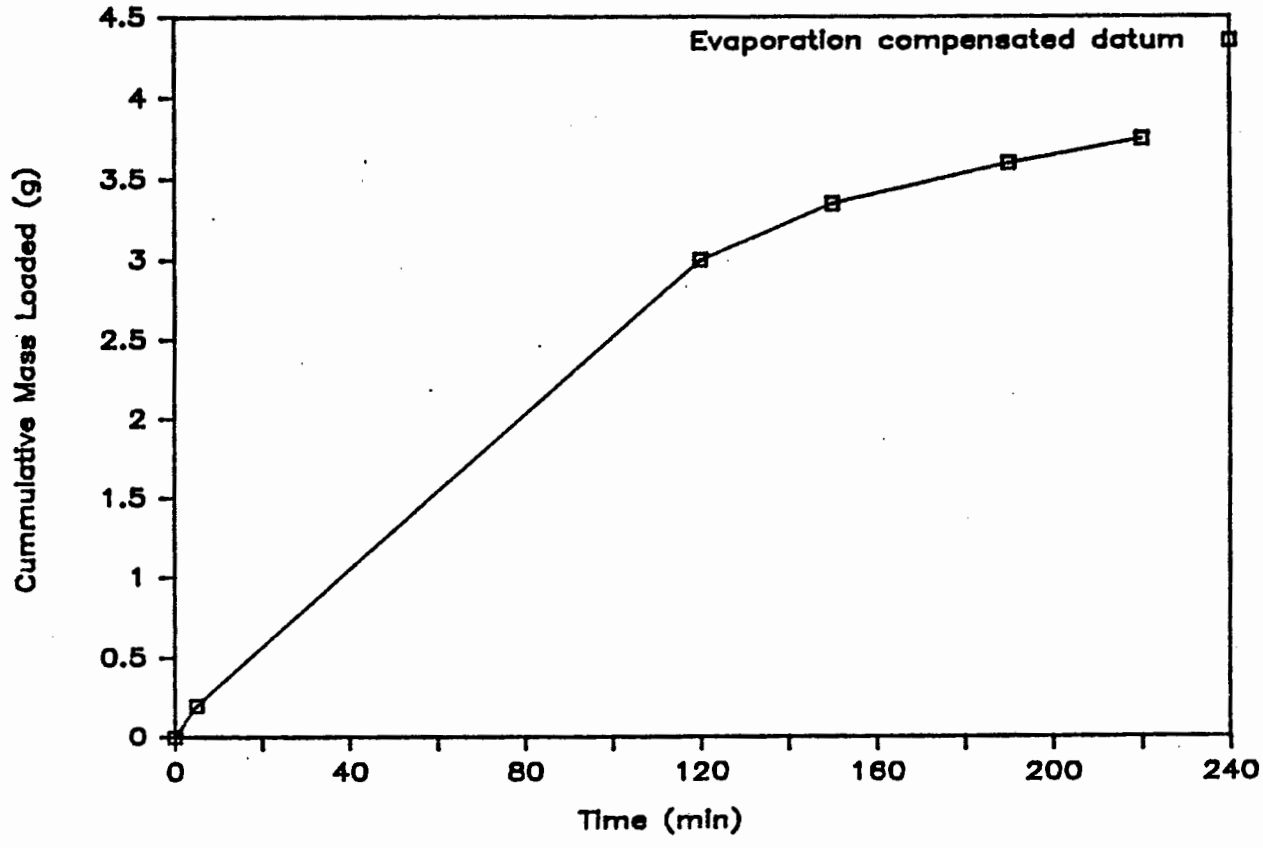


Fig. 2.2: Loading curve for cobalt complex adsorption onto activated carbon.

An aqueous solution of cobalt nitrate (45,06g $Co(NO_3)\cdot 6H_2O$ in 500ml distilled water) was used to slurry 48,82g of silica alumina (KC-Perlkator-D1; d < 500µm). The mixture was brought to the boil with stirring in a round bottomed flask with condenser system. Once simmering, 25g of urea was added. The system was left to reflux for 5h. After washing and drying, the cobalt content was found by A.A. to be 12,1 wt% Co. To make extrudates, 15g of kaolinite was mixed with 35g of the impregnated powder. Enough water was added to form an extrudable paste. $^1/_{16}$" extrudates were made. Harms (1987) reports that a mixture of 35 wt% kaolinite is more readily extruded.

2.1.5 Cobalt-SMM

Low cobalt content SMM catalysts were prepared by ion exchange. A 0,149 wt% Co was synthesized in the following procedure:
0,2923g $Co(NO_3)\cdot 6H_2O$ was dissolved in 100ml distilled water. 10ml of this solution was added to a further 790ml water. This solution was used to slurry 6,00g SMM (Harshaw/Filtrol) of particle size less than 212 micron. The SMM formed a suspension. The suspension was stirred at ambient temperature for 6h. It was necessary to extract the SMM by high pressure filtration (20 atm) and to maintain filter cakes of less than ca. 2mm thickness. The filter cake was dried at 80°C and then crushed.

The synthesis was repeated but a washing step was attempted. 500ml distilled water was added to the filter press once the original solution had been filtered off. Subsequent filtration took ca. 24h. The cobalt content was reduced to 0,139 wt%. Finally, a catalyst containing 0,04 wt% Co was synthesized by reducing the intial mass of $Co(NO_3)\cdot 6H_2O$ to 0,1074g and neglecting any washing steps.

2.1.6 Cobalt-Zeolite Y

Two different cobalt catalysts were prepared with this support. The first was prepared by ion-exchanging Co^{2+} ions for Na^+ ions in the lattice of Union Carbide Linde LZY-52 $^1/_8$" pellets. 15,02g LZY-52 was added to a solution of 40,072g $Co(NO_3)\cdot 6H_2O$ in 500ml distilled water.

The system was heated to 95°C and held at that temperature with stirring for 17h. This step was repeated a second time. Finally, the pellets were well washed with two half hour and one 6h washing in distilled water (ie., 3 by 500ml water). A.A. analysis of the pellets showed 5,64 wt% Co^{2+} ions and 5,27 wt% Na^{+} ions. This was equivalent to a 41,8% ion-exchange. A sample of this catalyst was soaked overnight in a excess of ammonia solution.

Similarly, cobalt was ion-exchanged with the protonated LZY-82 form. One catalyst of $^{1}/_{16}$" pellets had a cobalt content of 2,34 wt% while a powder version had 2,1 wt% Co.

2.1.7 Cobalt-NH_4^{+}-ZSM-5

The ZSM-5 support used in these catalysts was synthesized according to U.S. Patent 3702886 (Argauer and Landolt, 1972). The following chemicals were mixed in the stated proportions: tetrapropylammoniumbromide (Merc)- 31,13g; NaOH- 1,5999g; H_2O- 160,4g; $Al(OH)_3$ (Foseco)- 0,5588g. The solution was charged to an autoclave and heated at a rate of 1°C/min to 162°C. The temperature was held for 61h before cooling. The total yield of dry crystalls was 14,1838g. These were ascertained to have a Si/Al ratio of 12,96 and a crystallite size typically of 5 microns.

Detemplation of the batch was achieved by heating at 500°C under flowing ultra high purity nitrogen ($UHPN_2$) ($^{1}/_{8}$l/min) for 18h followed by 9h under air at the same conditions. To obtain the ammonium form, 10,8g of detemplated catalyst was added to 250ml 2M NH_4NO_3 solution in a glass reactor. The reactor was sealed and heated to 65°C where ion-exchange took place with stirring for 16h. The ion-exchange was repeated to ensure maximal NH_4^{+} content. The catalyst was filtered and dried after each exchange.

The cobalt NH_4^{+}-ZSM-5 catalysts were synthesized according to the method described by Stencel et al. (1983), ie., by incipient wetness impregnation. 1,6227g $Co(NO_3)\cdot 6H_2O$ was dissolved in 3,3ml distilled water and added to 6,5g NH_4^{+}-ZSM-5. The catalyst was dried at 80°C and

was analyzed by A.A. to have a cobalt content of 4,5 wt%. A 5g sample of this catalyst was washed with 1l of distilled water. This washing was in excess of the requirement that the filtrate lose its pink colour. The cobalt content was reduced to 1,1 wt%.

2.2 Experimental Rig

2.2.1 The Reactor

2.2.1.1 Reactor Selection

Many different types of integral flow through reactors have been used in the past for laboratory scale experiments. The sophistication of a reactor can be measured in terms of its ability to supply and remove heat. Ideally, the reactor should be able to transfer heat in such a way as to give an isothermal catalyst bed. Catalyst performance can then be correlated to an exact temperature. Simple tubular reactors enclosed in ceramic or metallic furnaces rely on conduction and low level convection from small surface areas. In the case of active catalysts, these reactors are well known to deviate strongly from isothermal behaviour. A wholly different approach is to do away with the furnace and use heat transfer fluids. These have markedly improved heat conduction properties. Air fluidised beds have been used succesfully by Imai and Uchida (1965) and by Harms (1987) to improve catalyst bed temperature profiles. It was thus decided to use a fluidised sand bath in the present work.

2.2.1.2 The Reactor Design

The reactor was simply a flanged stainless steel tube with a thermowell down its centre (see Fig. 2.3). The available volume within the reactor was 25ml and its dimensions were a length of 20cm and a diameter of 13mm. The thermowell contained three type J thermocouples to measure temperature at points 6cm, 12cm and 17cm down from the start of the bed. Both flanges could be unbolted. This had the merit of facilitating the

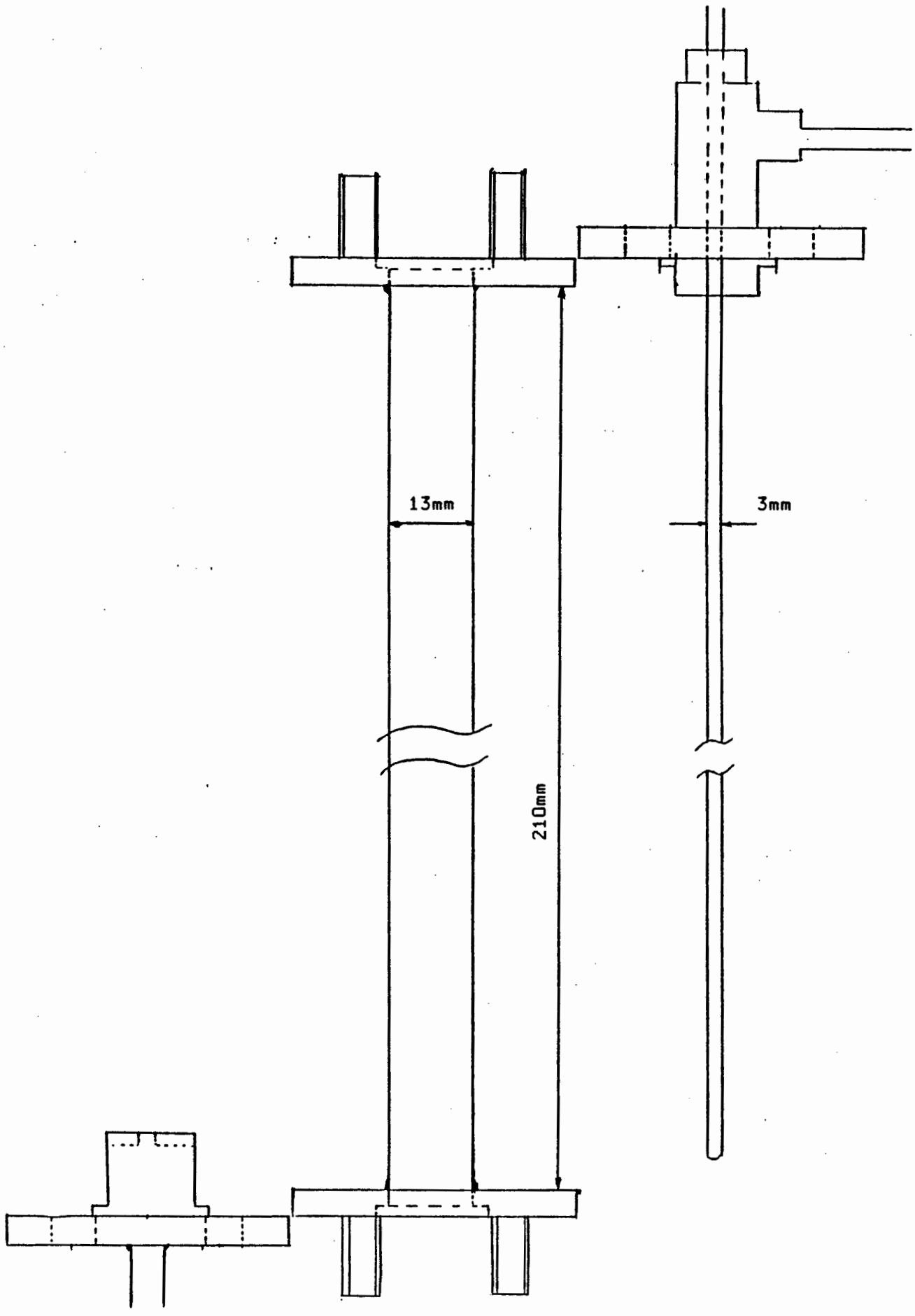


Fig. 2.3: Sketch of reactor assembly

cleaning and packing of the reactor. A disadvantage of having two flanges was that the probability of a leaking reactor seal was doubled. The flanges were however, successfully sealed by gaskets made of graphite with a nickel lamination (Flexitallic, UK). These gaskets were sealed in a recessed flange with corresponding mating male flange. A spiralled mineral insulated heating coil was wound around the outer suface of the tube. It was rated at 1,3kW.

2.2.1.3 The Fluidised Bath

The air fluidised sand bath was housed on a stainless steel tube 50cm deep and 14cm in diameter. A disengagement zone of 27cm was allowed for by the addition of a chimney at the top of the bed. A sintered brass disc served as a sparger. Its pore size was 150 microns and it was 0,5cm thick. An air pre-heat zone of 8cm was allowed for below the sintered disc. The entire sand bath was encased by a cylindrical mica band element of rating 2,2kW. This element had a maximum temperature limit of 400°C. The entire system was insulated with asbestos cloth and fiber glass. The fluidised bed was designed to be large enough to immerse the entire reactor and the hydrocarbon feed pre-heat section.

A useful feature of the fluidised bed was that the sand could be eluted by the insertion of an empty copper pipe into the bed. This phenomenon occurred only if the pipe contacted with the sintered disc and a preferential path created for air flow up the pipe. This phenomenon would not have occurred if the pressure drop across the sintered disc had been high enough that the pressure drop across the bed was negligible compared to that of the sintered disc. This technique could be used to drain the hot sand out of the bed after a calcination to facilitate rapid cooling.

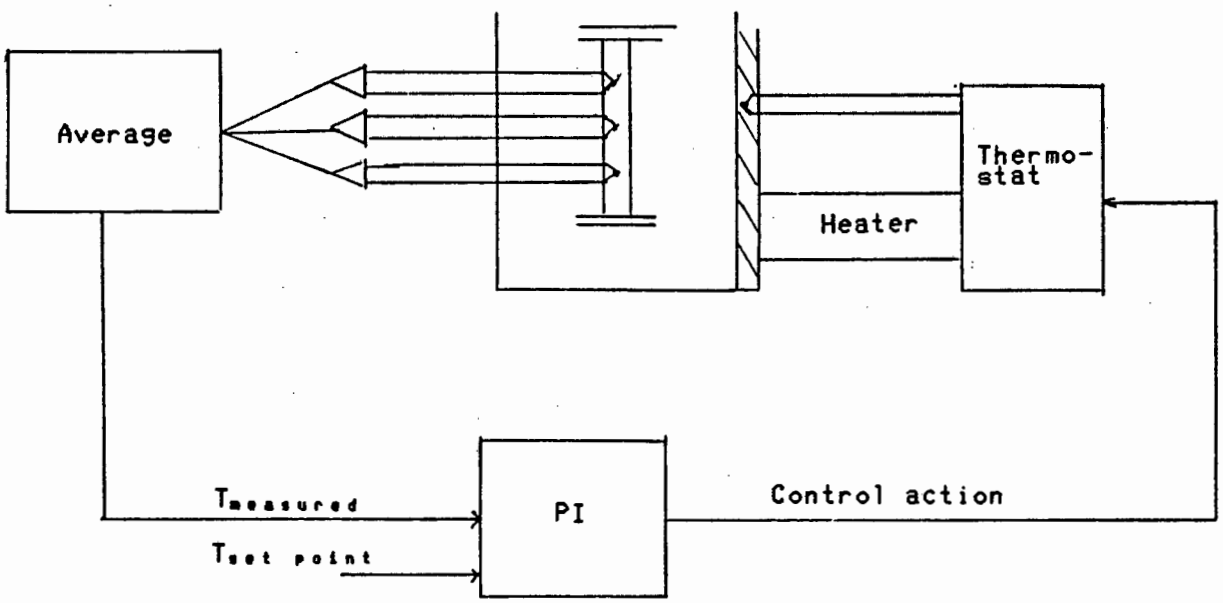
2.2.1.4 Temperature Control

The temperature control for this reactor required careful consideration. For temperatures in the range ambient to 400°C, the mica band element could be used to heat the sand bath. This supplied relatively isothermal

conditions for the reactor. Where higher temperatures were required, the spirally wound element was used to raise the temperature above 400°C. As a result of the upward flow of air, the reactor experienced a sharply increasing temperature profile. Since all reactions were run below 400°C, the mica band element was used to control reaction temperature. Thus any temperature profile would be due to heat of reaction.

During a reaction, it had previously been found (Harms, 1987) that the sand bath could be as much as 20°C below the catalyst bed temperature. A problem observed during the gradual deactivation of a catalyst was the corresponding drop in reactor temperature. An in house proportional-integral (PI) controller was designed to compensate for this problem.

FIGURE 2.4: Reactor control strategy.



The basic strategy for the reaction temperature control was as follows: The operator had to raise the temperature of the sand bath manually until the reactor reached the desired setpoint. This was achieved by a simple on-off controller with the controlling thermocouple in direct contact with the mica band element (to ensure immediate response). Once a fairly steady state was obtained, an automatic PI control loop could be introduced. The PI controller simply compared the average bed

temperature with the desired setpoint. If a discrepancy occurred, the setpoint of the thermostat was adjusted.

In designing the control system, it was found that a significant dead time lag existed between a step change in the mica band element temperature and the reactor temperature. This implied that the control loop was potentially unstable. Hence the PI controller constants had to be set to give slow controller dynamics. This sluggish control was found to be acceptable since the rate of deactivation of a catalyst was generally slow enough.

Temperature measurement was undertaken by the use of type J thermocouples. To manipulate the millivolt signals from these thermocouples, special operational amplifiers (AD594, Analogue Devices) were used. These had the merits of ice-point compensation built into them and the output voltage could be read as an actual temperature. Further, these voltages were in the useful range for the various electronic operations of averaging and integrating. A draw back of these chips was the fact that at high temperatures an offset developed. All data was adjusted accordingly.

The PI controller consisted of a series of operational amplifiers as shown by the circuit schematic shown in the Appendix. The tuning of the PI controller was achieved by varying the resistance and capacitance associated with the integrator and the resistors of the multiplier (ie. the proportional term). In order to obtain a large time constant (of ca. 100 seconds) for the integrator, a 25μF capacitor was required. When associated with the input resistance of 4,7M ohms, leakage through the capacitor became significant. This resulted in an unavoidable offset between the inputted setpoint temperature and the resultant reactor temperature.

During the commissioning of the rig, several control tests were performed. Fig. 2.5 illustrated the ability of the controller in the event of a step decrease in the reactor temperature. This was achieved by allowing the reactor to reach steady state and then passing a high

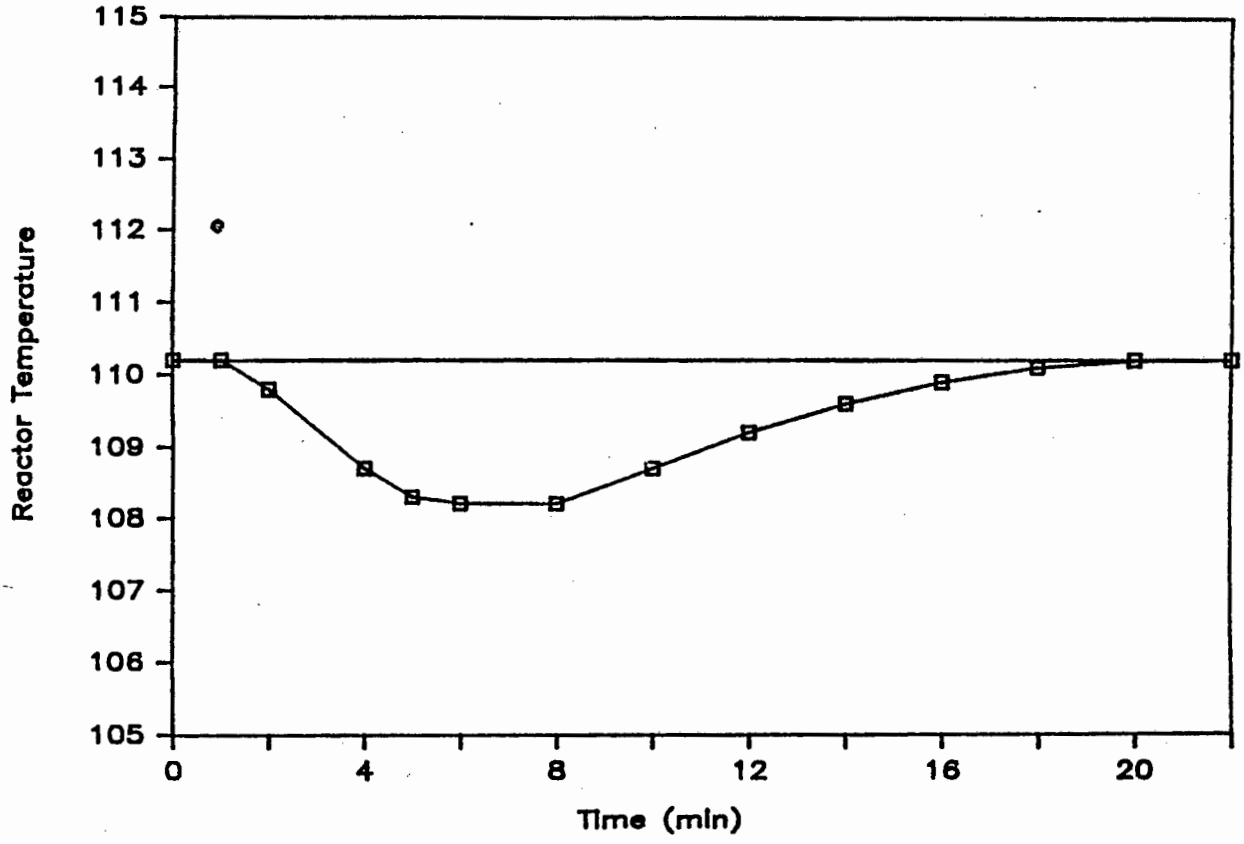


Fig. 2.5: Illustration of PI controller action.

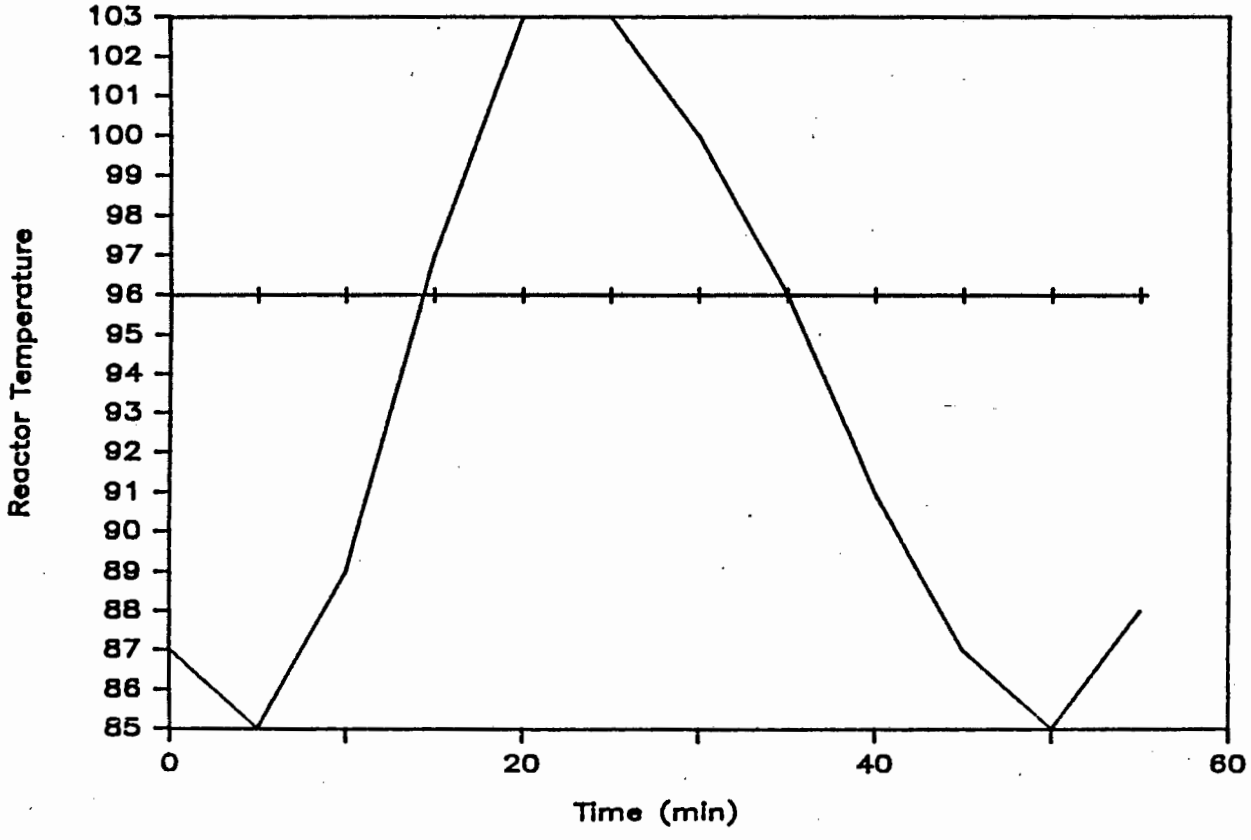


Fig. 2.6: Illustration of potential control loop instability.

flow of air through the reactor. This was considered to be a worst case as far as catalyst deactivation was concerned. The choice of PI controller constants was seen to be good. Fig. 2.6 illustrates the inherent instability in the control. The reactor temperature is seen to be oscillating wildly about a setpoint. It also indicates the need for the operator to have thermally stabilised the reactor before switching to PI control.

2.2.2 Reactor Rig Flow Description

The purpose and makes of all units shown in Fig. 2.7 are discussed here. Units are discussed in the flow sequence.

The hydrocarbon feed , typically an 85/15 wt% mixture of propene/propane was stored in a no.7 Cadac gas cylinder. The cylinder was connected to the rig via Swagelok quick-fit connectors. The gas bottle could be heated with an heating tape and controller. The feed then passed through two water traps each containing 30g of 3A molecular sieves (Merck). These sieves were regenerated before each experiment. The feed was then pumped upto reaction pressure using a Lewa FLM1 diaphram pump. This pump was capable of delivering flowrates from 18g/h to over 100g/h. The pump valves consisted of ruby ball and seat arrangements. These were very vulnerable to dirt and a 5 micron stainless steel sieve on the inlet was thus essential.

The hydrocarbon feed was passed through the reactor in which both calcination and reaction took place. Thereafter was a condenser to cool the hydrocarbon stream. The rig pressure was maintained by a Grove Mity Mite back-pressure regulator. A physical sieve was also essential to protect this unit. The back-pressure regulator was heated with warm water (ca. 45°C) to prevent freezing due to the flashing of the hydrocarbon as it depressurized.

The gas/liquid hydrocarbon mixture was disengaged in a catchpot and condenser system which were both cooled by glycol refrigerant at 10°C. The liquid was drained from the catchpot periodically. The flue gas was

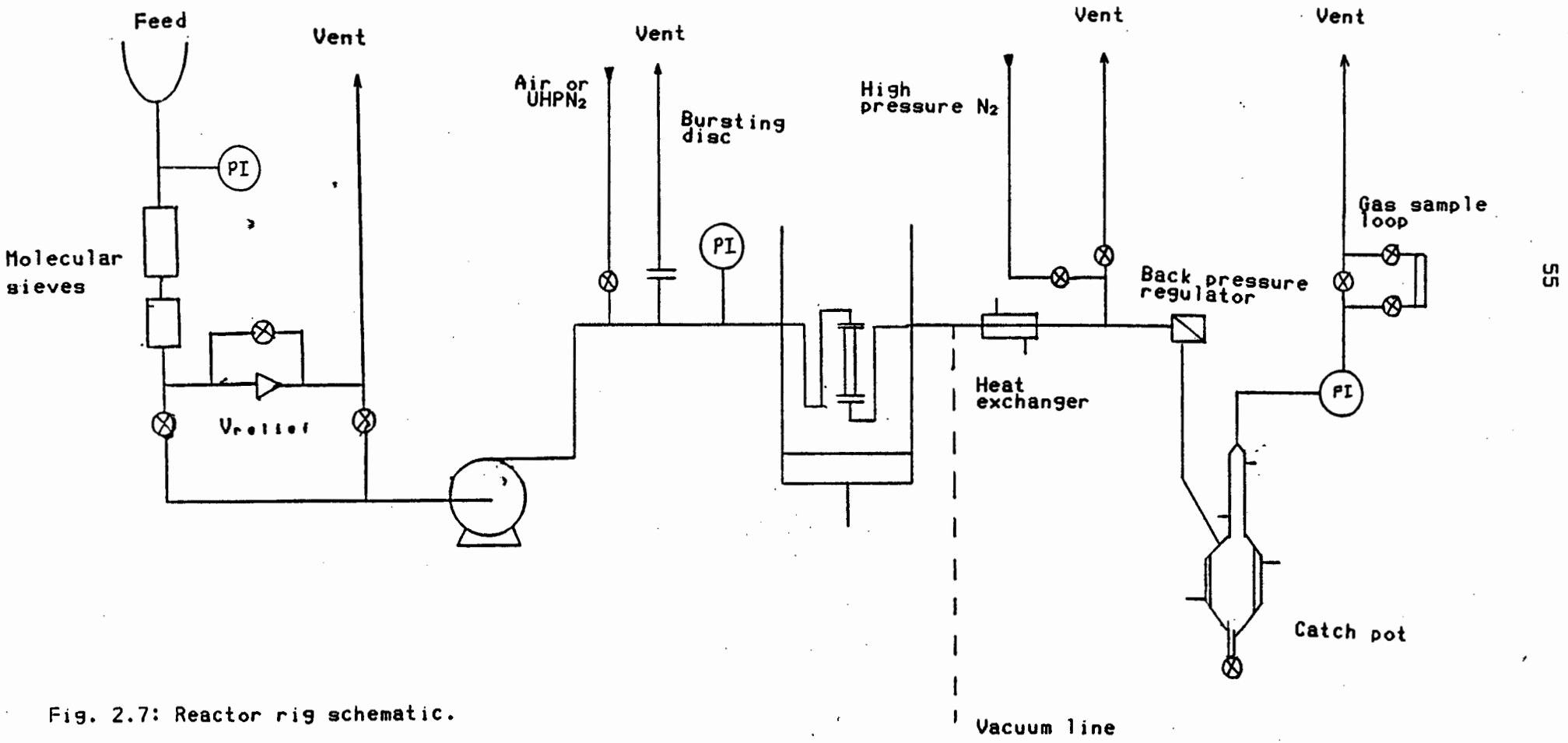


Fig. 2.7: Reactor rig schematic.

passed through an Alexander Wright Wet Gas Flow Meter and gas sample loop before being vented.

Safty features included a bursting disc rated at 70 atm (± 10% at 25°C) and a pressure relief valve for the gas bottle (set at 19 atm).

2.3 Experimental Procedure

This section outlines the procedures for packing the reactor, calcining and reacting over the various catalysts and finally for calculating the various reaction variables.

2.3.1 Packing the Reactor

The following table lists the usual masses of the various catalysts packed:

TABLE 2.1: Typical masses of catalyst packed.

Catalyst	Mass (g)
Co-carbon	3,0 or 1.5
Co-Si/Al	variable
Co-SMM	3,0
Co-ZSM-5	3,0
Co-NaY	3,0

The Co-carbon catalysts were diluted with 2mm glass beads. A typical dilution was 1 vol cat: 6 vol beads. The dilutions were uniform as the activated carbon granules were of similar dimension to the glass beads. This was also true for the zeolite Y pellets and the silica alumina extrudates. The powdered catalysts were less successfully diluted with the beads. At worst, the powder would fill up the voidage of the bed of glass beads. This was generally considered to be more desirable than a plug of pure catalyst.

The actual packing procedure was to bolt together the top flange, plug the top of the reactor with glass wool and then pour in the catalyst/glass bead mixture. Another plug of glass wool was inserted before the base flange was sealed. For the case where a catalyst slug was required, the symmetric sequence of glass wool, glass beads, catalyst, glass wool, glass beads and finally glass wool was adopted.

2.3.2 Calcination Procedures

The following table outlines the typical calcination conditions for the various catalysts:

TABLE 2.2: Typical calcination conditions.

Catalyst	Temp.(°C)	Time(h)	Medium	Pressure	Flowrate(ml/min)
Co-C	250	2	UHPN_2	3 mmHg	120
Silica alumina	380-470	7	Air	Atm	120
SMM	470	4	UHPN_2	Atm	100
Zeolite Y	380	6	UHPN_2	Atm	100
ZSM-5	470	26	Air	Atm	100

The packed and sealed reactor was heated to the specified calcination temperature by manual stepping of the temperature over typically 2,5h. The catalyst was held at that temperature for the given time and was exposed to the calcination medium at the given flowrate and pressure. The gases used had the following specifications (Afrox):

TABLE 2.3: Calcination gas specifications.

Impurity	HPN_2	$UHPN_2$	Air
O_2(vpm)	10	3	20,5-21,5(%)
H_2O(vpm)	10	5	15
CO_2(vpm)	ns	0,5	500
CO(vpm)	ns	0,5	10
NO_x	ns	0,1	ns
Min. purity(%)	99.995	99,999	ns

ns: not specified.

These gases were further dried with 3A molecular sieves which were renewed before each run.

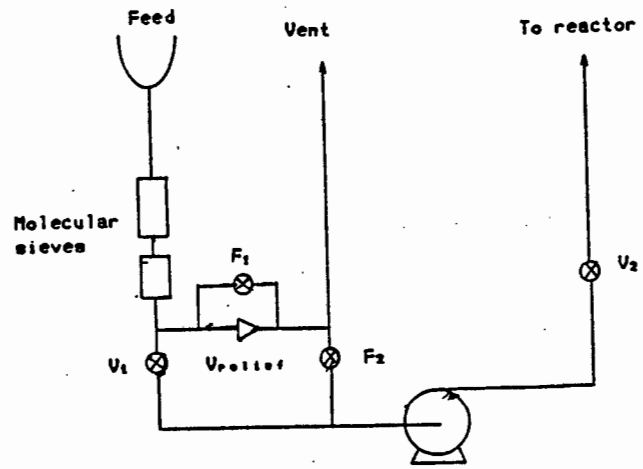
For the vacuum calcinations, the reactor outlet was connected to a flexible vacuum hose. The exhaust stream from the vacuum pump was used to set the nitrogen bleed flowrate. At the end of the calcination, the reactor was allowed to cool to ca. 70°C before the vacuum was gradually released by flooding the reactor with $UHPN_2$. The vacuum hose was then disconnected from the reactor with the $UHPN_2$ flowing continuously out of the reactor. After reconnecting the reactor outlet to the rig, the flow of $UHPN_2$ was continued to flush out that part of the rig which had been exposed to the atmosphere. Finally, the reactor was pressurised to 4 atm with $UHPN_2$ for overnight storage.

All calcinations were ended with the reactor being pressurised to 4 atm with the same gas used during the calcination.

2.3.2 Reaction Procedures

In order to ensure a dry feed, the following start-up procedure was adopted:

FIGURE 2.8: Start-up flow diagram.



The Cadac bottle was opened; flare valves F1 and F2 were briefly opened to flush out trapped air; the hydrocarbon was then left to dry overnight. V1 was cracked open and the hydrocarbon bled through the pump to V2. The hydrocarbon pressure would be 15 atm due to the gas bottle being heated to 40°C . The reactor was then equalised to this value using HPN_2. The pump was now primed with dry feed and V2 could opened and pumping commenced. From then onwards the hydrocarbon would pass through the molecular sieves at a rate which would give a dry feed (Jacobs, 1987). Based on the figures of Harms (1987), the wet feed had a water content of 51ppm. Making the conservative estimate that the molecular sieves have a moisture capacity of 2% of their mass, then the sieves would be able to dry 12kg of feed or the equivalent of a 600h run at a SV of 20g/h.

The feed was allowed to reach the reactor before any heating was undertaken. This was done to avoid the possibility of temperature runaways. The operating pressure was 50 atm(g) throughout the work done in this thesis (with the exception of the metathesis reaction in 3.7.3). Typical reaction temperatures and WHSV used are outlined in the table below:

TABLE 2.4: Typical reaction conditions.

Catalyst	Temperature(°C)	Average WHSV(g/h·g)
Co-C	40, 70	variable
Co-Si/Al	70, 180	variable
Co-SMM	70, 130	8,5
Co-ZSM-5	70, 180, 130, 270, 330	6,5
Co-NaY	85, 150-180, 230	variable

It was observed that the WHSV varied during a run. Initial variations were considered to due to temperature equilibration within the pump-head and the release of HPN_2 trapped in the rig by the startup procedure.

2.3.4 Calculation Procedure

The primary criterion for accepting the validity of a particular experiment was that a mass balance with losses less than 10% be obtained. It was thus essential that good procedures be adopted in calculating the various values for the balance.

All mass balances were started when the first drop of liquid was observed in the catchpot. The balances were terminated when the conversion reached a suitably low value. Two mass balance were required by this method when the hydrocarbon phase boundary was crossed (ca. 96°C).

The following definitions were adopted in this work:
* Space velocity (SV) = the mass of feed delivered per hour.
* Weight hourly space velocity (WHSV) = the space velocity per gram of catalyst.
* Liquid productivity (LP) = the mass of liquid produced per hour per gram of catalyst.
* Conversion (x) = the percentage of propene reacted and was calculated by the formula:

$$x = \frac{(1-C_g)\cdot LP}{C_3 \cdot WHSV} \cdot 100$$

where C_3 = the mass fraction of propene in feed

C_g = the mass fraction of dissolved gases in the liquid product.

* Percentage mass loss = the percentage difference between the mass lost from the feed cylinder and the sum of the liquid produced and the gas vented.
* Mass of gas vented was calculated using the ideal gas law but a compressibility factor of 0,986 was introduced.

2.4 Analytical Procedures

2.4.1 Catalyst Analysis

The primary analytical procedure for determining the cobalt content of the aluminosilicate catalysts was that of atomic absorption spectroscopy (A.A). This procedure required that the catalysts be totally dissolved. This was achieved by treating typically 0,25g of catalyst with 10ml of 48% hydrofluoric acid and in some cases 10ml conc. nitric acid. Once dissolved, the solutions were made upto 250ml in plastic volumetric flasks. A Varian SpectrAA-30 Atomic Absorption Spectrophotometer was calibrated using standard liquids from Spectrosol and was used to analyse for cobalt. The A.A flame emmision settings used were:

TABLE 2.5: A.A. settings.

Fuel: acetylene		
Support: air		
Wavelengh:	i) 240,7nm	ii) 304,4nm
Spectral Band Pass:	i) 0,2nm	ii) 0,5nm
Co ppm ranges:	i) 0-10ppm	ii) 50-250ppm

Varian publication No. 85-100009-00 reports that few interferences have been found in cobalt A.A. All cobalt contents reported via this method are reported as a percentage of the total catalyst mass.

The carbon supported catalysts were more problematic as the activated carbon did not dissolve in acids. Attempts to leach out the cobalt were unsatisfactory. Detailed analysis was not considered to be essential - the incipient wetness impregnation ensured that virtually all of the metal containing solution was adsorbed into the pores of the activated carbon. Low losses to synthesis vessels could thus be expected. The high metal loading also implied that a small loss was not significant. As explained in the synthesis procedures section (2.1.2) for the cobalt complex catalyst, cobalt loading could be deduced by mass balance. Nevertheless, samples of the above two catalysts were sent externally for X-ray Fluorescence Spectroscopy (XRF) analysis. Values of 10,4 ± 1,4wt% Co (or 13,2 ± 1,8wt% CoO) were obtained for this one off test. This analysis was in accordance with the assumption that nearly all cobalt was adsorbed by the carbon.

A Stanton Redcraft Thermo-gravimetric/Differential Temperature Analyser was used to investigate the nature of some of the catalysts. The influence of variables such as thermal stability, optimal calcination temperatures and times and the finger printing of virgin catalysts could be addressed. The coke content of spent catalysts could also be measured. All runs were undertaken with the following settings:

TABLE 2.6: TG-DTA settings.

catalyst mass:	ca. 20mg
heating rate :	10°C/min
medium :	NPN_2 or Air

Final temperatures and holding times were variable.

2.4.2 Hydrocarbon Gas Analysis

The propene/propane feed gas and the reactor effluent gas were analysed by a Gow Mac Gas Chromatograph 750P linked to a Varian 4270 integrator. The column used was a 3m $^1/_4$" stainless steel column with n-Octane/Poracil C packing. The G.C. settings were as follows:

TABLE 2.7: Gow Mac settings.

Gas flows:	N_2:	41ml/min
	H_2:	30ml/min
	Air:	300ml/min
Temperatures:	Injector	: 150°C
	Detector	: 250°C
	Column	: 50°C (isothermal)
Column Pressure	: 30psig at 50°C	
Sample Volume	:10µl	

The G.C. was calibrated using standards from Afrox. The following table show a typical feed analysis and the response factors for the gases generally found in the flue gas:

TABLE 2.8: Feed composition and response factors.

Component	Feed(wt%)	RF
Ethane/Ethene	0,21	1,024
Propane	13,35	1
Propene	86,44	0,971
N-Butene		1,056
Iso-Butene		1,002
T2-Butene		0,994
C2-Butene		1,029

Response factors were determined by the usual methods found in any standard text (McNair and Bonnelli, 1968). In most instances, the 10°C

trap system ensured that no significant quantities of heavier gases were present in the flue gases. Where conversion was over 90%, traces of C_5 and C_6 hydrocarbons were carried through. These accumulated in the column and regular conditioning at 120°C was necessary.

2.4.3 Liquid Product Analysis

Two gas chromatographs were available for liquid analysis: the first was a Varian 3400 containing a 3,5m $^1/_4$" glass column packed with 3% OV101 on Chromosorb W-HP; and the second was a Varian 3700 containing a 30m fused silica mega-bore column of I.D. 0,25mm and coated with 25 micron layer of DB1. Both G.C.'s were linked to a Varian 401 Data System for integration. Each had the following settings:

TABLE 2.9: Data for liquid G.C. analysis.

	OV101-Chromosorb	Megabore
Detector:	F.I.D	F.I.D
Gas Flows: N_2-	30ml/min	27ml/min make-up flow 3ml/min column flow
Air-	300ml/min	200ml/min
H_2-	30ml/min	30ml/min
Temperatures: Injector-	250°C	250°C
Detector-	300°C	250°C
Column programs:	40°C(5min), 10°C/min to 180°C, 30°C/min to 300°C(5min)	35°C (5/8min), 10°C/min to 275°C (6min)
Pressure:	18psig at 40°C	6psig at 35°C
Sample volume:	0,3µl	0,1µl

Liquid product spectra are reported for the various reactions in the results section.

The liquids produced in this work contained enormous numbers of isomers. One ZSM-5 sample was analyzed by G.C. as having over 300 separable

components. Attempts to identify all of whese peaks would be time consuming and not necessarily meaningful except in the event of an exceptionally dominant peak. The second best alternative was to use G.C. to identify groups of hydrocarbons. In the case of pure oligomerization, the oligomers were clearly identifiable. Where cracking occurred simultaneously, the groups merged and it was impossible to discern groupings. However, G.C./Mass Spectrophotometry could be used to obtain approximate groupings. For example, in the case of the aluminosilicate catalsts, a trimer was defined to consist of C_8, C_9 and C_{10}. Since the degree of branching strongly affects the boiling range of a C_n group of isomers, overlap of these groups inevitably occurred. However, such groupings gave a good indication of the mass distribution of the liquid between light and heavy ends. Also, comparisons could be made between liquid products of modified catalysts.

The above mentioned groupings should be determined for the product of each catalyst tested. This is a result of the fact that different catalysts have different favoured reactions and products. These different product spectra could affect the grouping boundaries. It was found that groupings defined by GC Mass Spec. for SMM matched the chromatogram for ZSM-5 and silica alumina well at the low temperature reaction conditions where oligomers were clearly visible. Since GC-MS was not readily available, it was assumed the these groupings still applied in the presence of cracking. The groups used are listed below and they apply to the packed column discussed below:

TABLE 2.10: Oligomer groupings for OV101 column.

Oligomer	Interval
Monomer C_1-C_4	0-1,02 min
Dimer C_5-C_7	1,02-4,70 min
Trimer C_8-C_{10}	4,0-11,2 min
Tetramer C_{11}-C_{13}	11,2-15,7 min
Pentamer C_{14}-C_{16}	15,7-18,5 min
Hexamer C_{17}-C_{19}	18,5-20,5 min
Heptamer C_{20}+	20,5-28 min

Since Co-C catalysts gave clearly defined oligomer groups, the oligomers could be grouped exactly. The C_{12} group and above was not distinguishable but was insignificant in terms of quantities detected. Since the Co-C liquid product was predominatly dimer, an attempt was made to separate the C_6 isomers. A standard solution containing ca. 1% each of 11 commonly otained isomers was made up on an octane solvent. At 20°C, the megabore was able to separate the 9 groups although the important isomers in the range 67-68°C (see Table 2.11 below, ex CRC Handbook, 63rd Ed.) lay as a peak with 2 close shoulders. The pure product was more difficult to separate. One large peak (ca. 30% of the product) straddled the above shouldered peak. Also the response time was not linear with respect to peak size. In the absence of a longer capillary column, the C_6 isomer identification was abandoned. A product spectrum in the Appendix shows the 5 predominant C_6 isomer groups separable by megabore. The distribution was found not to vary with runtime or between different catalysts.

TABLE 2.11: C_6 isomers.

Isomer	Boiling Point(°C)	Heat of Formation(kcal/gmol)
3 methylpent-1-ene	51,1	-11,02
4 methylpent-1-ene	53,9	-11,66
C-4 methylpent-2-ene	56,3	-13,26
t-4 methylpent-2-ene	58,5	-13,26
2-methylpent-1-ene	60,7	-13,56
1-hexene	63,3	-9,96
c-3-hexene	66,4	-11,56
t-3-hexene	67,1	-12,56
2-methylpent-2-ene	67,3	-14,96
c-3-methylpent-2-ene	67,6	-14,32
t-2-hexene	68	-12,56
c-2-hexene	68,8	-11,56
t-3-methylpent-2-ene	70,4	-14,32

2.4.4 Ultra violet (U.V.) Spectrophotometry

A Varian SuperScan 3 Spectrophotometer was used in the synthesis of the activated carbon supported $Co(NH_3)_6(NO_3)_3$ catalyst. The U.V. was used to positively identify the complex by its characteristic response at 473nm. Further, it was calibrated with known solutions and was then used to generate the complex loading curves shown in Fig. 2.2. The scanning range was 530-430nm at a rate of 50nm.

3 RESULTS

3.1 Preliminary Investigations of Cobalt-Carbon Catalysts

This section outlines the preliminary work done in order to gain an understanding of the nature of the cobalt-carbon catalyst. Different combinations of cobalt and carbon were first tested. Then, a simple impregnated catalyst was made and tested. Since the catalyst system proposed first by Schultz et al. (1966) appeared to be the most stable of those reported in the literature, attempts were made to reproduce their work. A double ammoniated cobalt on carbon catalyst was synthesized and tested. This was selected as a base case. Variations to this basic synthesis were examined at varying operating conditions.

3.1.1 Tests on Combinations of Cobalt and Carbon

Pure activated carbon was calcined at 260°C under vacuum and nitrogen bleed for 4h. No oligomerization activity was observed at 60°C or at 210°C under 50 atm of feed. Laboratory Co_3O_4 powder was calcined at 285°C in HPN_2 for 2h. Again, no reactivity was observed at 60°C. Thirdly, a physical mixture of activated carbon and Co_3O_4 was similarly tested and found to be inactive. Finally, pure activated carbon was soaked in conc. ammonia solution. After drying and calcining at 260°C under flowing High Purity Nitrogen (HPN_2) and partial vacuum, the ammoniated carbon was tested for oligomerization activity and was found to be inactive.

3.1.2 The Performance of a Non-ammoniated Catalyst

To assess the effect of the ammoniation procedure of Schultz et al. (1966), a non-ammoniated catalyst was synthesized. 12,1g of $Co(NO_3)_2 \cdot 6h_2O$ was dissolved in 13,5ml of H_2O. This solution was added to 20g of WCM106 activated carbon. No excess fluid was present. The catalyst was dried on a hot plate with stirring for 30 min.

10g of this catalyst was activated and tested. Operating conditions of 50 atm pressure and a feed WHSV of 2,2h^{-1} were selected. The reaction was initially autothermal with the fluidizing air being used to keep the temperature as low as possible. On contact with feed, the temperature rose rapidly from 27°C to 55°C but fell below 40°C in 2 min. The bed temperature was subsequently maintained at 33°C. Over the first 21 min 1,02g/gcat•h were produced. In the ensuing 31 min the production dropped to 0,41g/gcat•h. No further liquid was observed and a subsequent temperature increase to 70°C did not rend further activity to the catalyst. The liquid produced in the first 21 min had a composition of 64% dimer, 25% trimer and 11% tetramer+.

3.1.3 The base case

This section describes an oligomerization experiment which formed the basis against which further preliminary tests were measured. The synthesis and calcination of this catalyst are described in detail in section 2.3.

9,9g of undiluted catalyst was packed into the reactor. Upon start up of the experiment, a maximum temperature run-away of 60°C above ambient was observed. This peak lasted 2-3 min before decreasing. By controlling the fluidising air flow and sand bath temperature, the average bed temperature was driven up to 70°C. The reactor conditions were held at 70°C and 50 atm. An average feed weight hourly space velocity of 2,7h^{-1} was maintained (Fig. 3.1). The run was terminated when the rate of liquid product formation reached 27% of the initial value after 6,5h. The total liquid produced was 9,4g/gcat with a maximum conversion of 88%. When the run was repeated, the second experiment gave a 9% increase in total liquid and a 0,5h increase in lifetime. The agreement between runs was considered to be good. The product spectrum was typically 77% dimer, 20% trimer and 3% tetramer.

3.1.4 Variation of Operation Variables

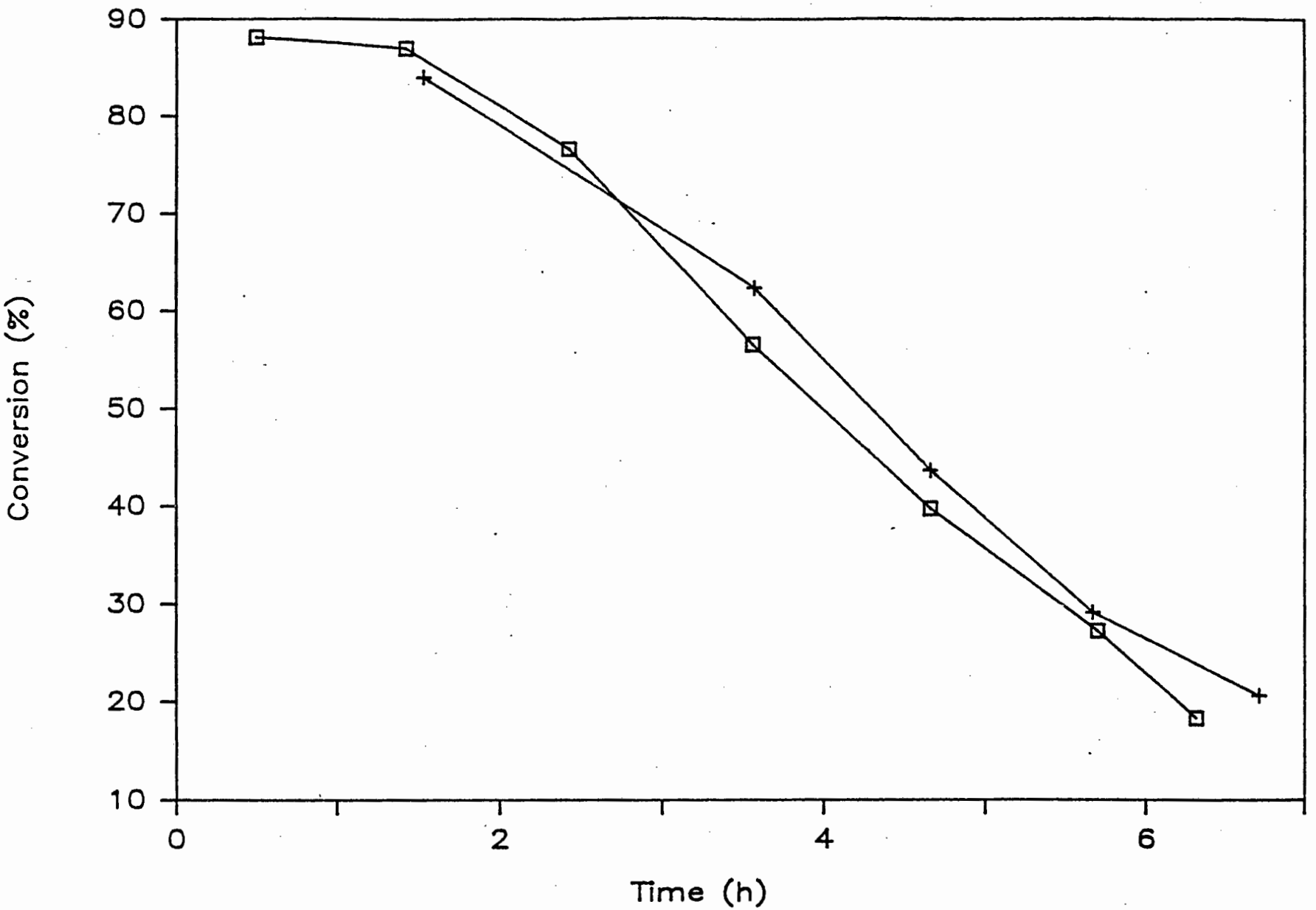


Fig. 3.1: The base case.
Catalyst = CoOCSP2 (9,9g), WHSV = 2,7h^{-1}, Pressure = 50 atm, Temp. = 70°C.

i) Industrial N_2 vs HP N_2

In the calcination procedure, industrial N_2 (4500 vpm O_2 and 50 vpm H_2O) was tried instead of HPN_2 (10 vpm O_2 and H_2O). Despite an increase of approximately 1,5 fold in the WHSV (to 4,3h^{-1}), the total liquid production still fell sharply from 9,4g/gcat to 2,35g/gcat (Fig. 3.2).

ii) Further O_2 and H_2O reductions

In the light of the above, it was decided to reduce still further the exposure of the catalyst to water and oxygen. Ultra-high purity N_2 (UHPN_2: 3 vpm H_2O and 3 vpm O_2) was used for calcination. A celite oxygen trap was also installed in series with the feed drying molecular sieves. The oxytrap was synthesized as follows (McIlurick and Phillips, 1973) : 24g celite was slurried with 48g of analytical grade hydrated manganese acetate in 72ml methanol. The slurry was dried and the catalyst packed in a pre-reactor with approximately the same volume of 2mm glass beads. The acetate was then decomposed at 400°C in air and the resultant oxide subsequently reduced in H_2 at 400°C. This system had been reported/patented for the removal of low concentrations of O_2 from gas streams and it was hoped that it would do the same in the hydrocarbon stream. No analytical equipment was available to measure the O_2 content of the feed steam.

To test the effect, two experiments were carried out where 12,3g of the same undiluted catalyst (CoOCSP3) was packed in the reactor and calcined. In both cases, the catalysts were calcined by heating to 260°C and holding for 1,5h. Here the calcination was initially only under partial vacuum (0,28mmHg) with 120ml/min UHPN_2 bleed being introduced an hour before the end of the hold period (the pressure rose to 3mmHg).

Both runs were operated at a pressure of 50 atm and WHSV of 3,1h^{-1}. Difficulty was experienced in maintaining the temperature at the desired value of 40°C. The run without the traps was maintained in the range 36-40°C whilst the run with traps fluctuated between 40-50°C (See 3.1.8 for discussion on reactor performance). The results of the two runs are plotted in Fig. 3.3. Total liquid productions were 31,1g/g for the control run and 33,6g/g for the run with traps. This 7% diference was

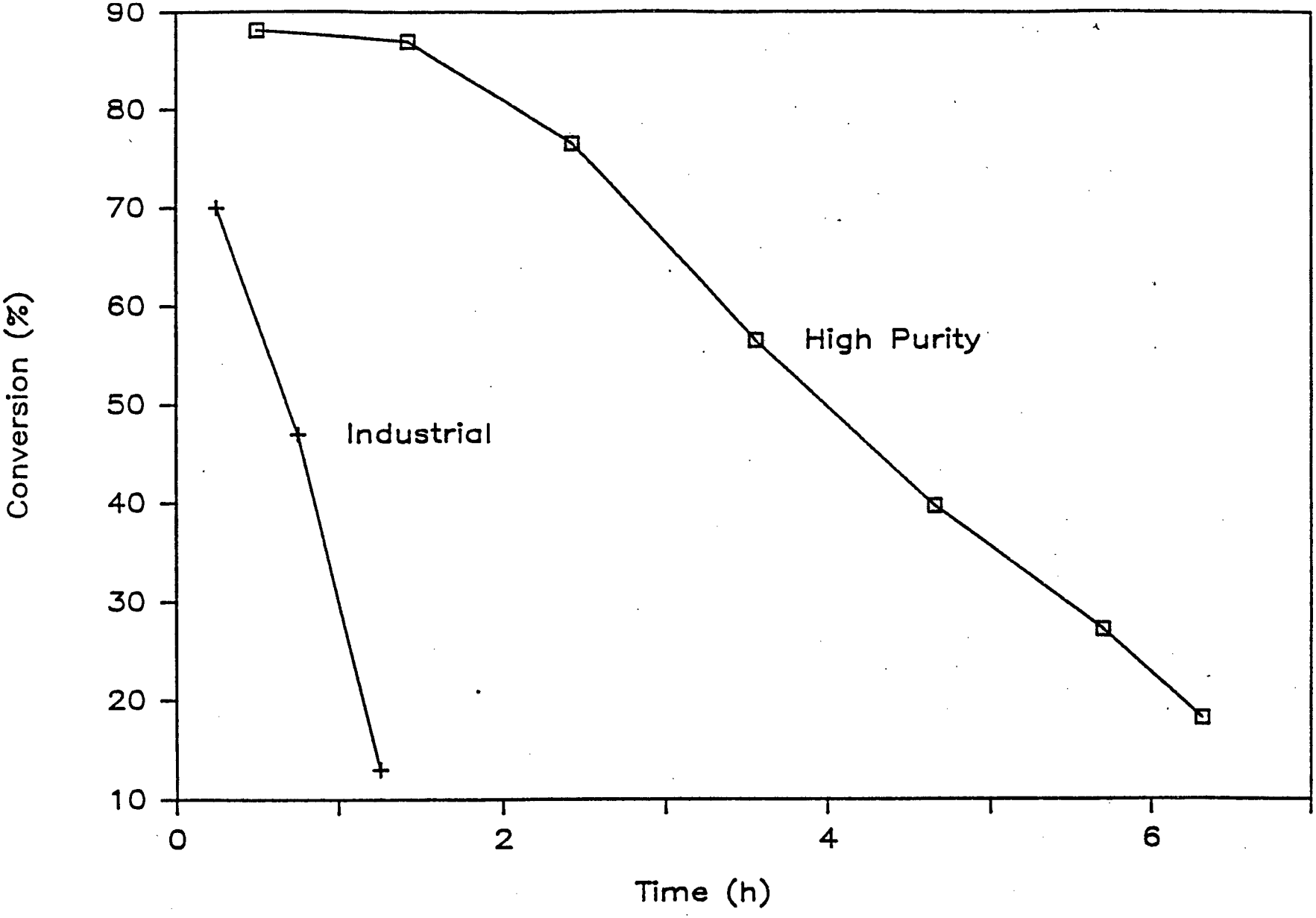


Fig. 3.2: The effect of calcination N_2 purity.
High Purity: Catalyst = CoOCSP2 (9,9g), WHSV = 2,7h^{-1}, Pressure = 50 atm, Temp. = 70°
Industrial: Catalyst = CoOCSP2 (5,6g), WHSV = 4,3h^{-1}, Pressure = 50 atm, Temp. = 70°

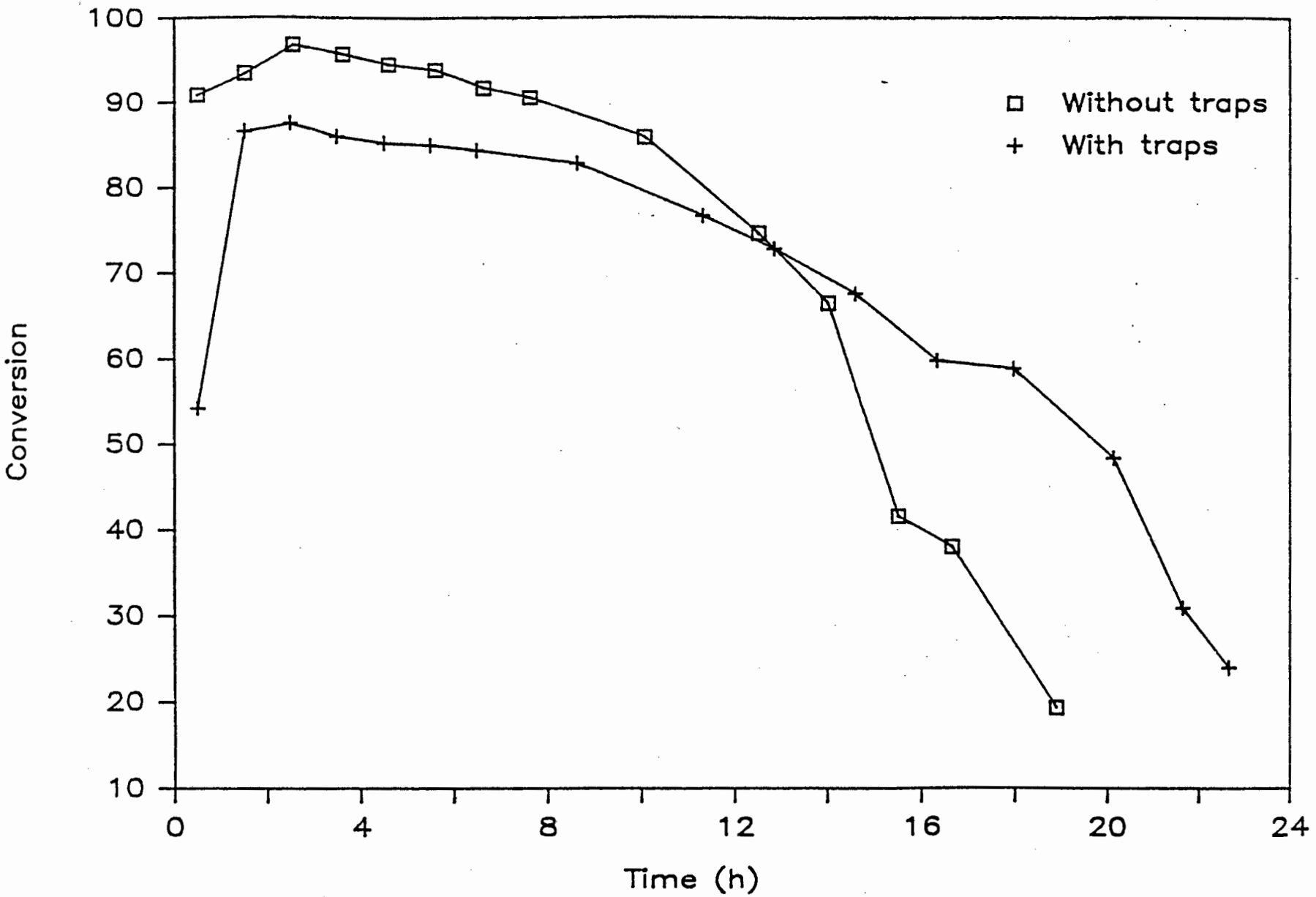


Fig. 3.3: The effect of oxy-traps.
Catalyst = CoOCSP3 (12,3g), WHSV = 3,1h^{-1}, Pressure = 50 atm, Temp. = 36-50°C.

within experimental error. Although the traps appear to have decreased the initial activity, the lifetime was improved. This could however, have been the result of the temperature difference in the runs.

Liquid product spectra showed little variation. The initial spectra are shown in Table 3.1:

TABLE 3.1: Liquid spectra showing the effect of oxy-traps.

	With traps	Without traps
Dimer(%):	76	73
Trimer(%):	20	22
Tetramer(%):	3	4

Compared to the base case (CoOCSP2) which produced 9,4g/g liquid at a WHSV of $2,7h^{-1}$, this new value of 31,1g/g (by CoOCSP3) was an improvement. The differences between the two experiments were that:
a) the latter was operated at a lower temperature (36-40°C vs. 70°C);
b) the pre- and post-ammoniation treatments of CoOCSP3 included an overnight soaking in ammonia solution. To clarify the cause of the improvement, it was necessary to re-run CoOCSP3 at the same temperature as the base case (iii below).

iii) Effects of Reaction Temperature and WHSV

As outlined in (ii) above, the oligomerization reaction appeared to be sensitive to relatively small variations in temperature. 3g of CoOCSP3 was calcined in the manner of the base case and reacted under the same conditions except for a WHSV increase to $5,8h^{-1}$. Fig. 3.4 shows the expected trends that the conversion was lower and the lifetime reduced. The total amount of liquid produced per gram of catalyst (ie., 9,4g/g) was exactly the same in both runs.

The fact that both runs produced the same quantities of liquid product per gram of catalyst does not imply that the performances of the

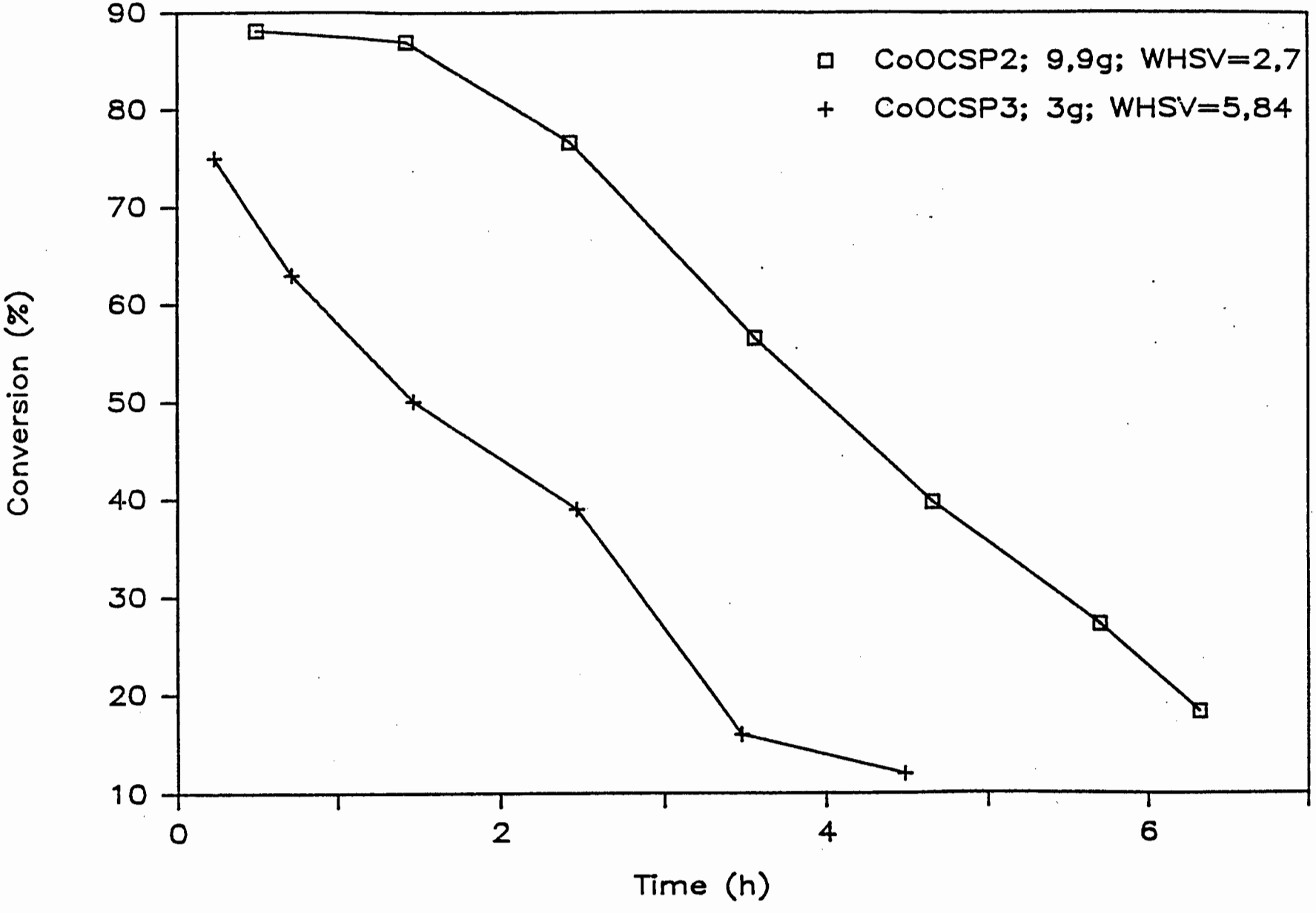


Fig. 3.4: A comparison between CoOCSP2 and CoOCSP3.
Pressure = 50 atm, Temp. = 70°C.

catalysts were identical. If the WHSV had been the same in these two experiments, it is possible that the total liquid production of CoOCSP3 at 70°C would have been less than that of CoOCSP2 at the same temperature.

These results show that a 30°C decrease in reaction temperature resulted in an increase in liquid product of at least 3,5-fold. It was possible that the synthesis modifications to CoOCSP3 (b above) did not necessarily improve the catalyst performance. Further investigation in this regard was clearly necessary.

3.1.5 Variations in Ammoniation Procedure

A paticular batch of catalyst (CoOCSP4) was synthesized with the following two modifications: i) the catalyst was dried at a pressure of 10mmHg (as apposed to 1mmHg); ii) the post-impregnation ammoniation was done while the catalyst was still hot (above 100°C) and immediately re-dried. This was undertaken since the literature synthesis procedure gave no indication of a treatment period. This catalyst was tested and found to be inactive. A sample of this batch was soaked overnight in 25% ammonia solution.

10g of the still wet catalyst was packed into the reactor without inert dilution. The heating period to 260°C was increased to 3,7h to allow for the fact that the catalyst was packed wet. It was held at 260°C for 3h and a vacuum of 10mmHg with 100ml/min UHPN_2 bleed maintained throughout. On account of the now high initial conversions obtained in the above reported runs, a higher average WHSV of 8,0h^{-1} was selected. This increase in WHSV was important as comparison between experiments is extremely difficult when conversions are high. For this run a pure propene feed was used. The temperature varied between 42-55°C. This fluctuation was due to control problems in trying to maintain the temperature of the undiluted catalyst bed with the fluidising air flow rate. Clearly this control strategy was unsatisfactory. Fig. 3.5 shows that the overnight soaking was effective in activating the catalyst. The ammoniation contact time was evidently an important variable.

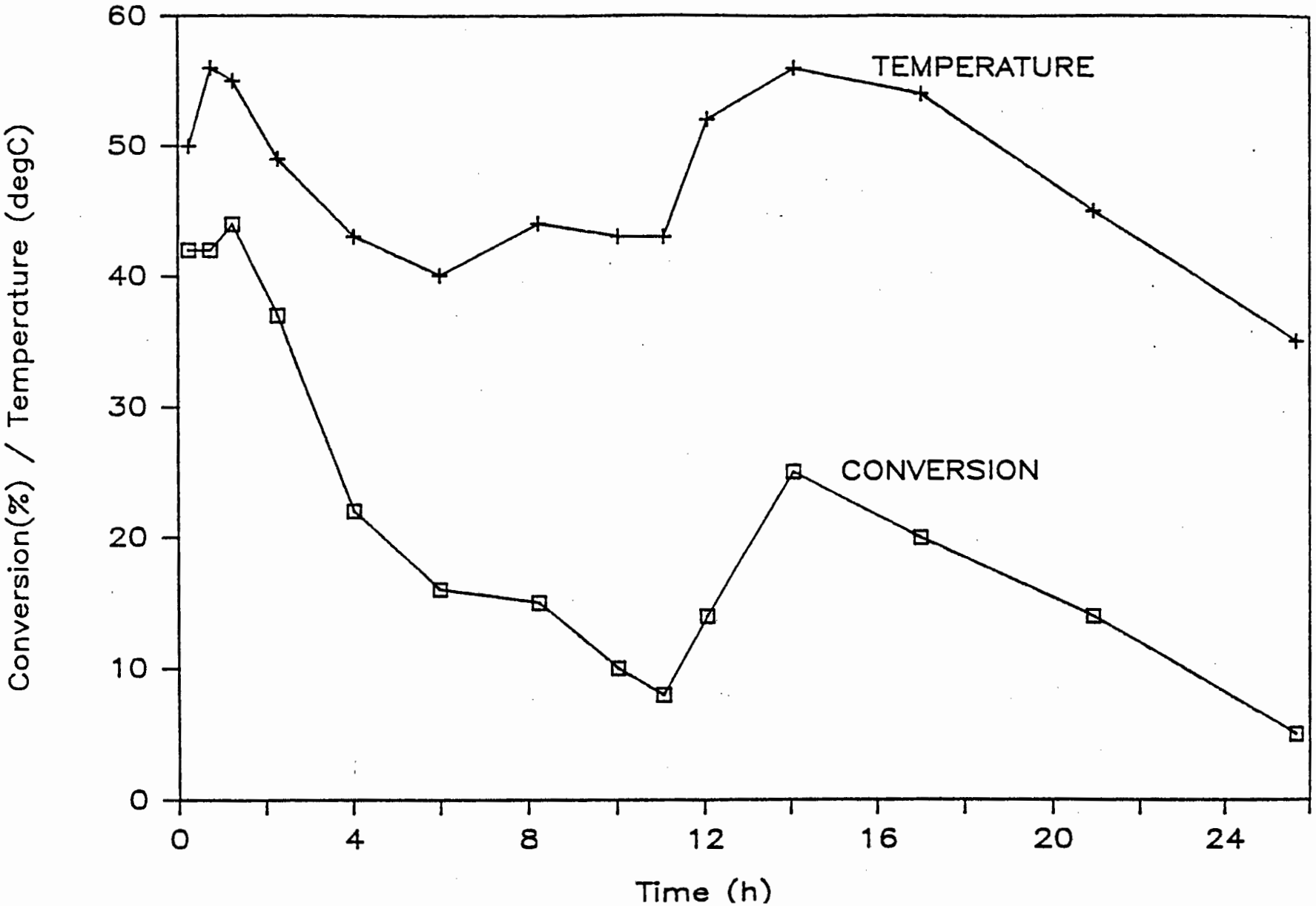


Fig. 3.5: The performance of CoOCSP4.
Catalyst = CoOCSP4 (10g), WHSV = 8.0h^{-1}, Pressure = 50 atm.

Since such a marked improvement was given by overnight soaking of the catalyst in ammonia, it was considered that an excess of ammonia in all steps could be essential. A catalyst was synthesized (CoOCSP5) whereby the initial activated carbon was soaked twice in ammonia solution and allowed to dry under ambient conditions. Further, after cobalt impregnation, the catalyst was dried first at 80°C for 5h and then at 110°C for 8h under vacuum. The post ammoniation took the form of an ammonia soak. The catalyst was left for several hours before being packed wet into the reactor. The rationale here was to again do the post ammoniation drying and calcination simultaneously.

Schultz et al., 1966 operated their oligomerization reactions at high WHSV and obtained high liquid yields and lifetime. The WHSV was controlled to maintain a conversion of ca. 10-20%. This approach was adopted in testing the above catalyst. 4g of wet catalyst was calcined exactly as above. As shown in Fig. 3.6, at an initial WHSV of 21,7h^{-1} and a reaction temperature of 40°C, the total liquid production was 8,8g/g over 9h - a marked reduction in performance.

3.1.6 Nitric Acid Pretreatments

As discussed previously, Schultz et al. (1966) found that a nitric acid pretreatment of the activated carbon was in fact equivalent to a pre-ammoniation. Dutch workers (Dutch Patent 6412392) found that this treatment was an important activator. Hence this treatment was tested. 20g of raw activated carbon was reacted with 50ml conc. HNO_3 and 50ml water for 20 minutes. Copious brown fumes were liberated. Impregnation was as in the base case and the post ammoniation consisted of an overnight soak and ambient evaporation to dryness.

This catalyst was tested under the conditions of 48-53°C, WHSV of 34h^{-1} reducing to 16h^{-1} as shown in Fig. 3.7. In 15,3h, a liquid production of 39,4g/g was obtained. This was deemed to be no better than a pre-ammoniated catalyst.

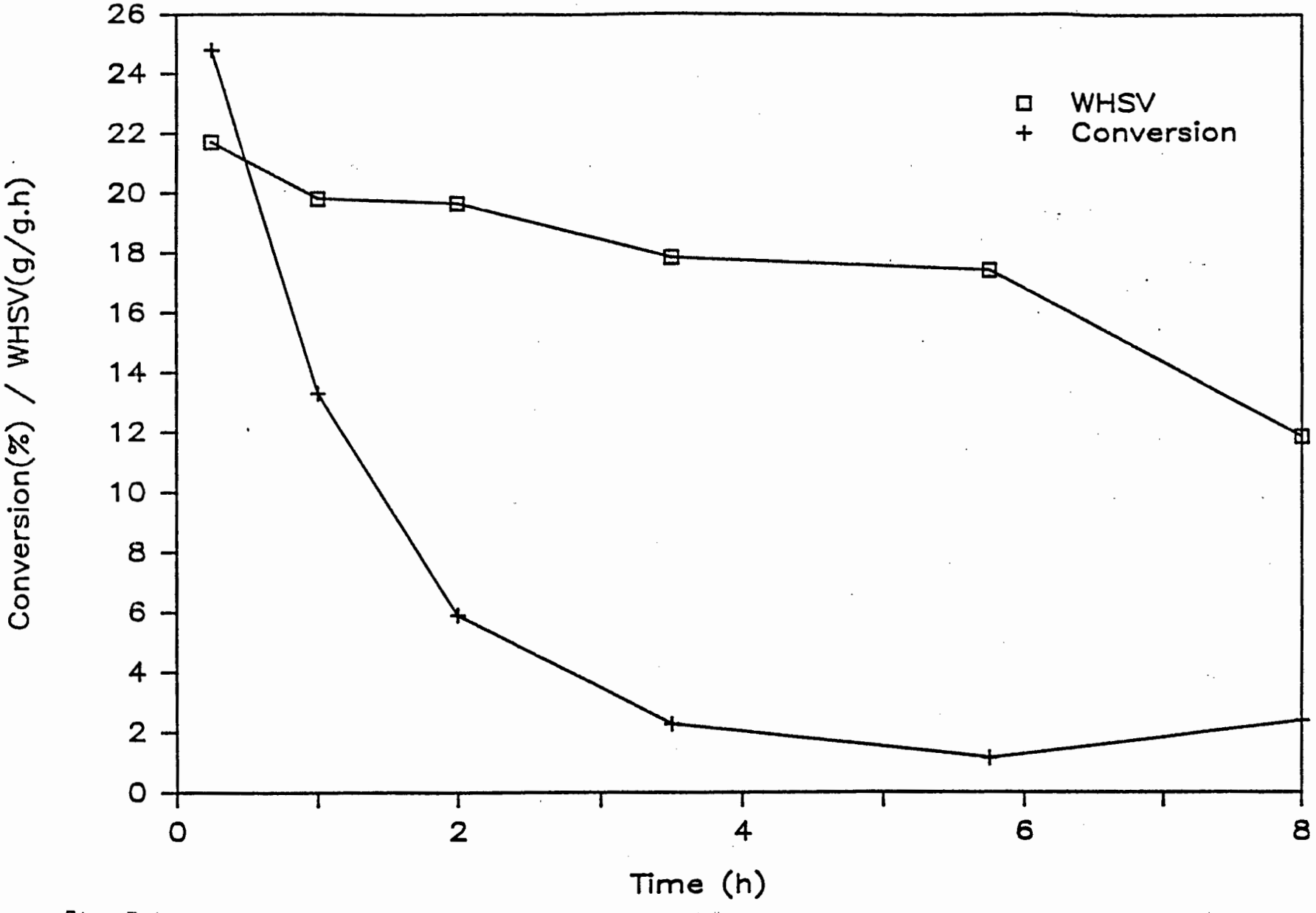


Fig. 3.6: The performance of CoOCSP5.
Catalyst = CoOCSP5 (4g), Pressure = 50 atm, Temp. = 40°C.

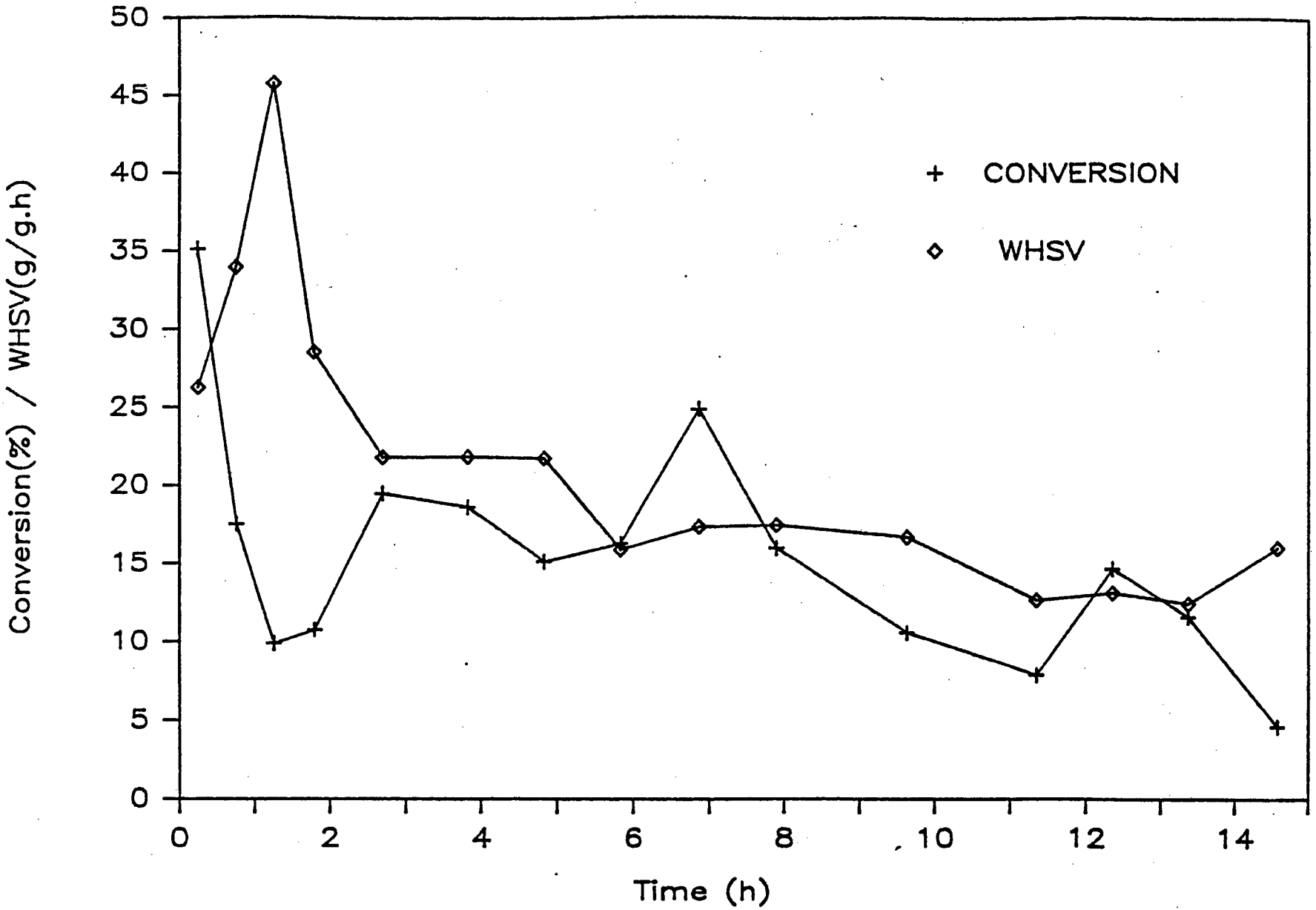


Fig. 3.7: The performance of a nitric acid pretreated catalyst.
Catalyst = HNO_3CoOCSP1 (3g), Pressure = 50 atm, Temp. = 48-53°C.

3.1.7 A Regeneration Attempt

The spent catalyst of the oxygen/water trap run (Fig. 3.4) was considered to be a good sample for a regeneration attempt - it had been on stream for a long period and was deactivated. At the end of the run, the hydrocarbons were flared from the rig and UHPN_2 was immediately passed over the catalyst at 130ml/min. The temperature was raised to 180°C over 2,5h and was held at that temperature for another 2,5h. Fig. 3.8 shows a typical thermal analysis of a spent Co-C catalyst. The analysis was done in flowing HPN_2 with a heating rate of 10°C/min. Clearly the above treatment would remove significant quantities of hydrocarbon.

The propene/propane mix was passed over the catalyst but no activity was observed.

3.1.8 Problems Related to Standardising Experimental Conditions

During the course of the experimental work on the cobalt-carbon system, practical difficulties were experienced reproducing reaction conditions. During initial probe experiments, ca. 10g of catalyst were packed in the reactor. This relatively large amount was chosen due to the initial low conversions and short catalyst life times obtained. Runs were carried out at ca. 70°C at which temperature the fluidized bed was capable of maintaining relatively isothermal conditions. However, as experiments advanced, the catalytic activity was improved. Further, the need to operate at ca. ambient temperatures was identified. The fluidized bed was not able to maintain isothermal conditions because of the low temperature difference between the reactor and the sand bath. As a direct result of varying ambient conditions, the equilibrium catalyst bed autothermal temperature varied from run to run. To improve the temperature profile in the bed, the catalyst was diluted with glass beads. Typically, 3g of catalyst were packed. Since the minimum space velocity available was ca. 18g/h, runs with 3g of catalyst had to have a minimum WHSV of ca. $6h^{-1}$. Hence comparison between results was complicated.

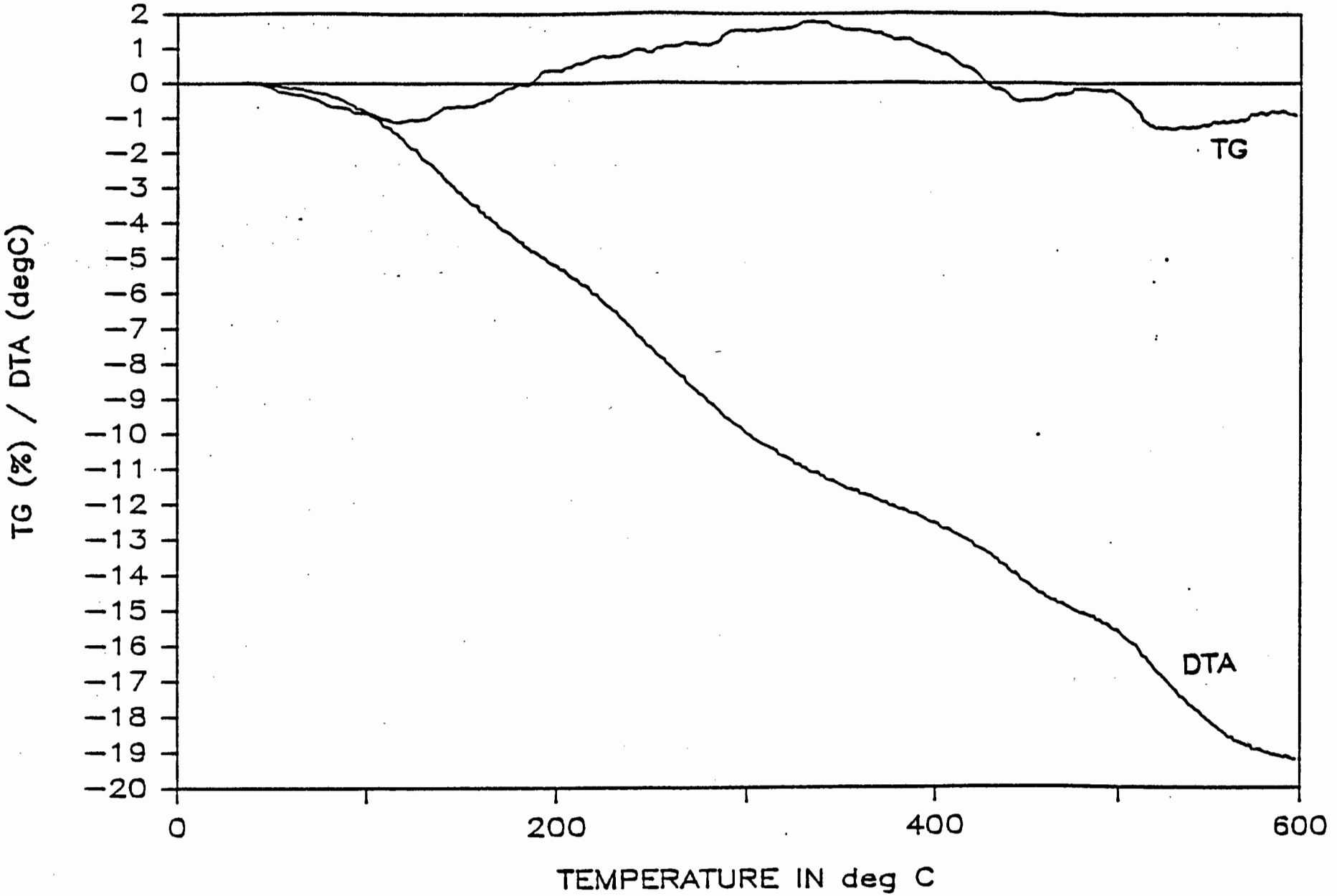


Fig 3.8: Thermal analysis of spent Co-C catalyst (heating rate = 10°C/min, atm. = HPN_2)

In spite of these difficulties, it was recognised that an ordinary jacketed reactor would in no way have been able to maintain reaction temperatures at the low values achieved in this work.

3.2 The Effect of Varying Post Ammoniation Contact Time

In the preliminary investigation, it became clear that the period of contact between the impregnated catalyst and the post-ammonia solution was of importance. To quantify this observation, a series of syntheses were undertaken in which the only variable was the post ammoniation contact time. The best catalyst was then tested under all the possible optimal conditions in an attempt to reproduce the long lifetimes (of the order hundreds of hours) observed by Schultz et al. (1966).

3.2.1 The Ammoniation Series

50g of activated carbon was pre-ammoniated with 80ml NH_3 solution by soaking overnight. This was followed by drying on a hot plate until visibly dry and vacuum drying at 150°C for 24h. 30,3 g of $Co(NO_3)_2 \cdot 6h_2O$ was then impregnated, dried for 4h and finally vacuum dried for 17h at 110°C. 70ml of NH_3 solution was added once the impregnated catalyst had been cooled. After time intervals of 35 min, 1h, 2h, 6h and 24h, samples were removed and dried on an oil bath until visibly dry (ca. 10 min). They were then vacuum dried at the same temperature. As a result of this procedure, the first sample could only be dried for ½h, the second for 1h, and the third for 4h. Since small samples were used (ca. 9g), they were all considered to be sufficiently dried. An unusual observation in this series was that the half hour treated sample had a milky blue colour on its surface. The rest of the samples were all black.

The oligomerization reaction was carried out over 1,5g of each of the above catalysts at 50 atm and 40°C. The propene/propane feed had 86,4% propene, 13,4% propane and 0,21% ethane/ethene. The catalysts were diluted with 2mm glass beads in the volumetric ratio 1:9. This high

dilution coupled with high WHSVs gave good temperature profiles (less than 4°C). The results of these runs are shown in Fig. 3.9. The WHSV's were in the range 12,5±0,5h^{-1}.

The catalysts showed an activity sequence 1h > ½h > 6h > 24h (refer Table 3.2). Evidently an optimum contact period existed. On account of the fairly narrow spread of curves, it was deemed unnecessary to optimise this variable. In subsequent syntheses, 1h was the selected post ammoniation contact time.

TABLE 3.2: Liquid production data for ammoniation series catalyst.

Catalyst	Total Liquid Production(g/g)
Co-C½hA	47,2
Co-C1hA	66,1
Co-C6hA	31,0
Co-C24hA	26,0

Since the 1h synthesis procedure was used in all subsequent work, it was useful to examine the liquid product spectra produced by this catalyst. Fig. 3.10 shows the liquid spectra as a function of time on stream. There was a slight shift to lighter products as the catalyst deactivated. The proportion of of the two major C_6 isomer groups (group 1 and 2 in Fig. 3.10 - see Appendix for discussion on these groups) remained unchanged. The final sample had a composition of 76% dimer, 21% trimer and 3% tetramer. This break in trend suggested that a desorption of trimer from the catalyst was occurring at a greater relative rate than was previously occurring. This could be due to a high concentration of trimer on the deactivated catalyst. It was considered unlikely that the effect was due to the dimerising sites coking at a greater rate than the trimerising sites - the liquid spectrum trend with time on stream would in that case have been a shift to heavier products.

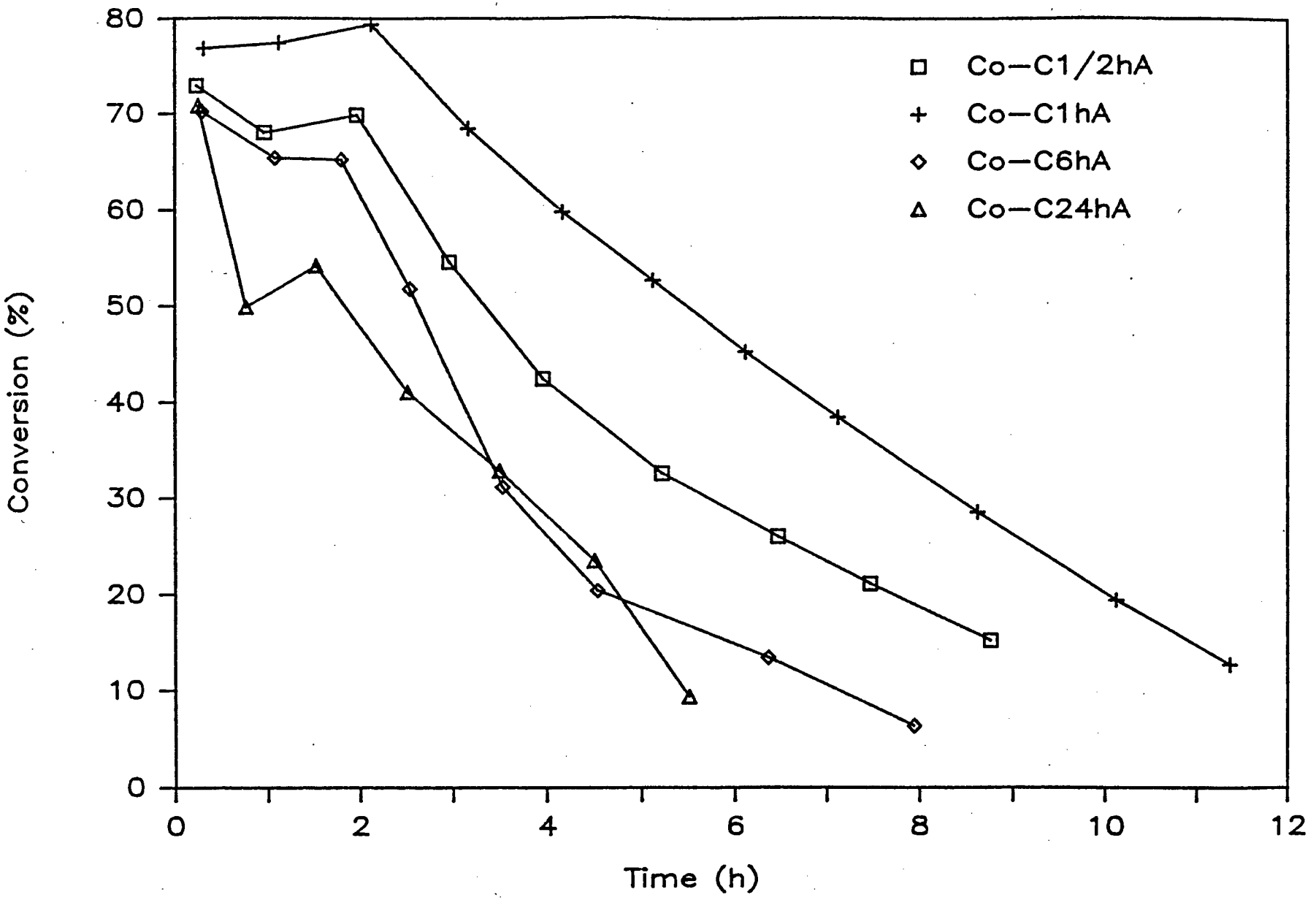


Fig. 3.9: The effect of varying post-ammoniation contact time.
Catalyst mass = 3g, WHSV = 12,5±0,5h^{-1}, Pressure = 50 atm, Temp. = 40°C.

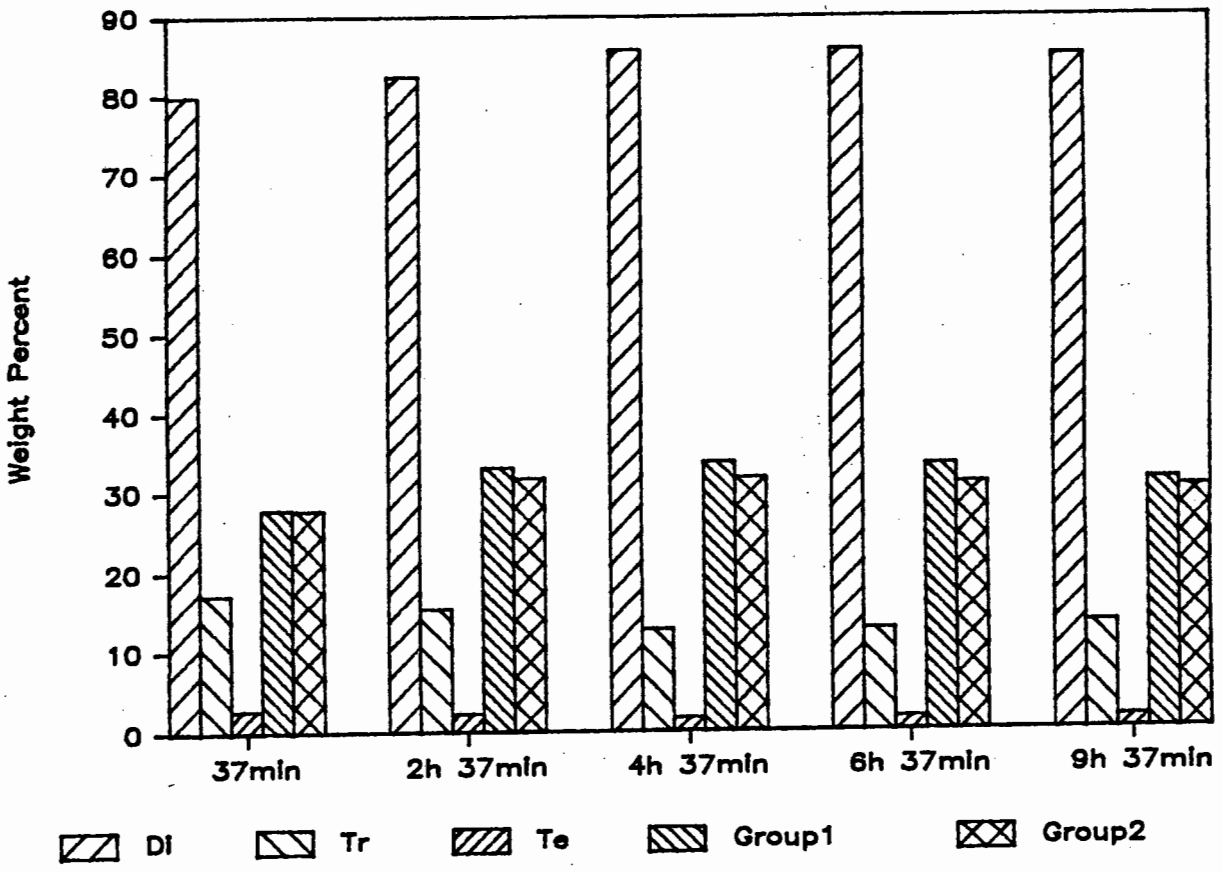


Fig. 3.10: Liquid product spectra of Co-C1hA as a function of run time. WHSV = 12,5±0,5h^{-1}, Pressure = 50 atm, Temp. = 40°C.

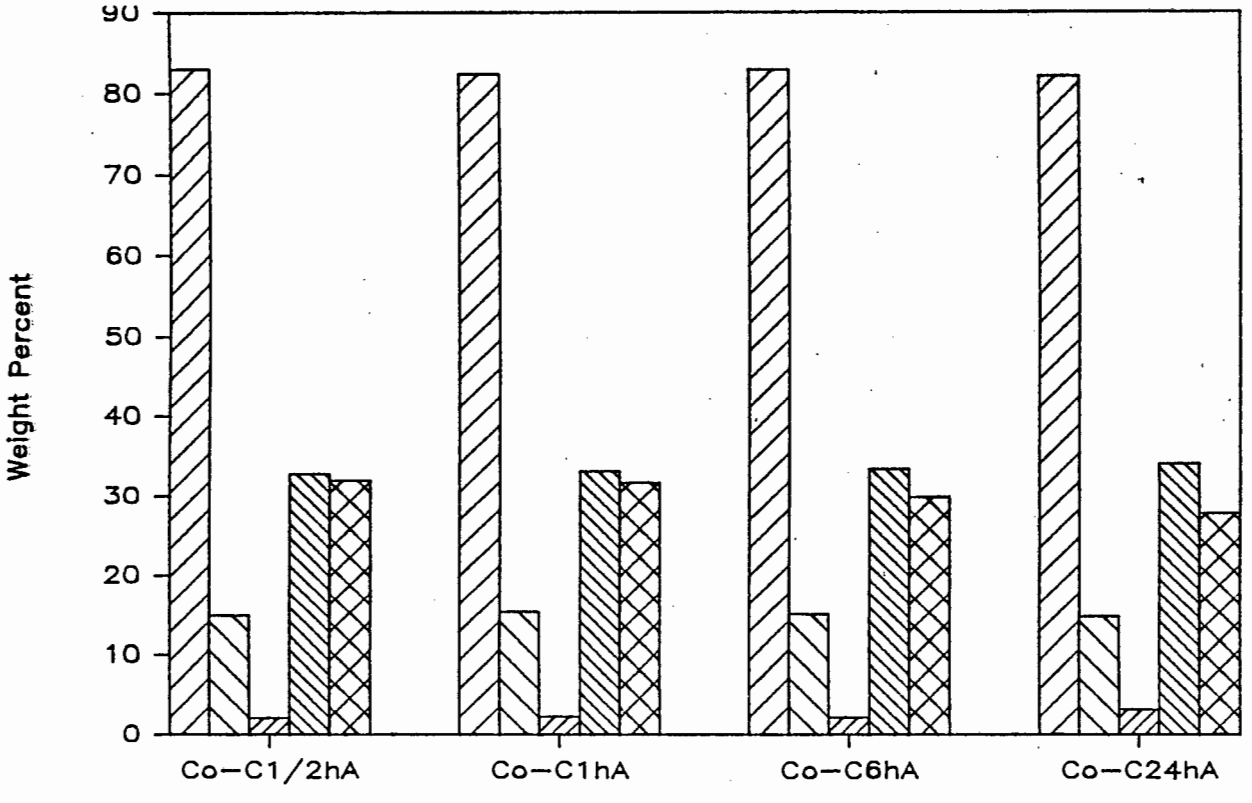


Fig. 3.11: Liquid product spectra of ammoniation series of catalysts. WHSV = 12,5±0,5h^{-1}, Pressure = 50 atm, Temp. = 40°C.

Fig.3.11 shows the product specta for the four runs after ca. 2,5h on stream. It is clear that little effect on product spectra occurred as a result of adjusting post ammoniation contact time.

3.2.2 Experiment at Optimal Conditions

The possibility existed that the calcination temperature and feed in the above experiments were not optimal. Hence the following experiment was undertaken: 1,5g of catalyst was calcined at 275°C for 2h under a partial vacuum (5mmHg with 120ml/min UHPN_2 bleed) - the optimal calcination temperature according to Schultz et al. (1966). Further, a feed of 99,9% pure propene was used. This would ensure that all conditions were similar apart from the WHSV which was maintained at the same value as the above experiments (12,5±0,5h^{-1}). Fig. 3.12 compares the two experiments with Co-C1hA. In spite of the higher initial conversion, the lifetime was not appreciable affected by the variations in feed and calcination temperature. It must be noted that the lack of inerts in this experiment implies that the propene feed rate is ca. 20% higher. The initial activity under these conditions was thus significantly higher.

3.3 Activated Carbon Surface Modifications

This section describes the results of the work done to test the effect of various activated carbon pre-treatments. It was hoped that these tests would elucidate the role played by the activated carbon activation procedure in the catalytic ability of the Co-C interaction. Also some indication of the need (or lack thereof) for oxygen functional groups on the surface of the activated carbon might be gained.

3.3.1 Oxygen Treated Activated Carbon

A batch of activated carbon was oxidised in flowing O_2 (refer 2.1.1). According to Boehm (1966), this procedure should give a maximally oxidised surface. A double ammoniated catalyst was sythesized with this

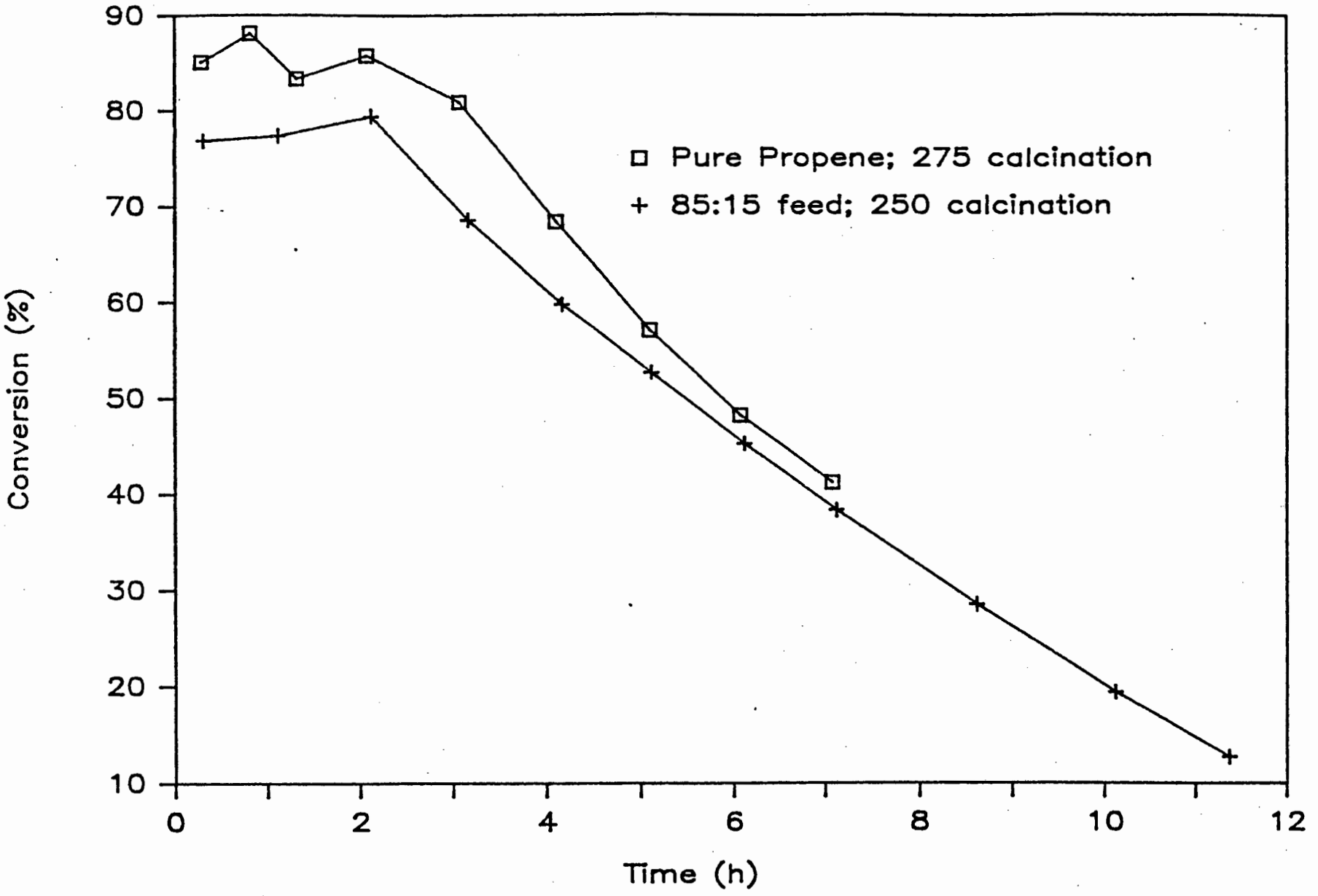


Fig. 3.12: The effect of a 275°C calcination plus pure propene feed on Co-C1hA.

activated carbon (Co-OC). The synthesis was identical to that described for the Co-C catalyst post-ammoniated for 1h (Co-C1hA)(See section 3.2).

1,5g of Co-OC was calcined as in Co-C1hA and run at 40°C with an average WHSV of 13,3h^{-1}. Fig. 3.13 shows the plot of conversion against time for the oligomerizing reaction. On the same graph is plotted the analoguous run but without the carbon pretreatment (average WHSV=13,0h^{-1}). Total liquid productions where 66,1g/g for the unoxidised catalyst and 62.6g/g for the oxidised version. The higher initial conversion and shorter lifetime of Co-OC suggested that this catalyst was more active initially but that the rate of deactivation was also promoted. The total liquid productions were considered equal within the limits of experimental error. Hence it would appear that no new sites were created by the O_2 oxidation but that the existing sites were more active for both the reaction and for coking.

A comparison of the liquid spectra (Table 3.3) indicated that no marked difference exists although the Co-OC product was fractionally heavier.

TABLE 3.3: Product spectra of O_2 oxidised activated carbon.

Catalyst:	Co-OC	Co-C1hA	Co-OC	Co-C1hA
Dimer(%):	78	80	84	86
Trimer(%):	18	17	14	13
tetramer(%):	4	3	3	2
Time on stream:	28 min	37 min	4h28 min	4h37 min

3.3.2 Hydrofluoric Acid Pretreatment

As described in section 2.2.1, a sample of activated carbon was treated twice with 48% HF. Ash analysis of the treated carbon showed that the ash content was reduced from 2,44 wt% to negligible proportions. Another potentially important factor was that the washing of the leached carbon

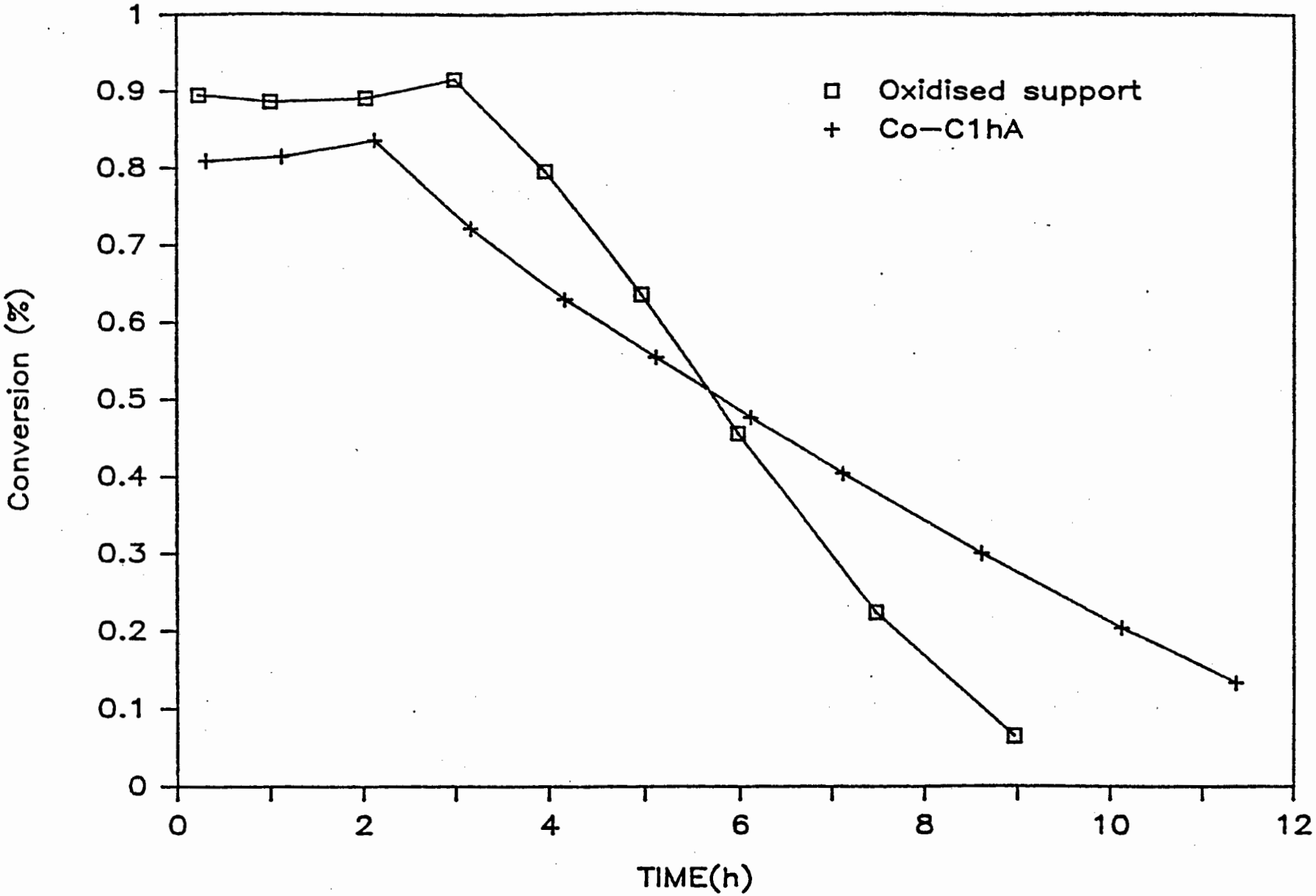


Fig. 3.13: The effect of oxidising the activated carbon with O_2.
Catalyst mass= 3g, WHSV = 12,5±0,5h^{-1}, Pressure = 50 atm, Temp. = 40°C.

was stopped at a stage when the pH of the washings was 4. Hence some of the HF must still have been present on the activated carbon.

The double ammoniated catalyst synthesized from this batch of activated carbon was made as follows. 10g of activated carbon was soaked overnight in 50ml of ammonia solution and then dried and vacuum dried at 120°C. The activated carbon was impregnated with 5,437g $Co(NO_3)_2 \cdot 6h_2O$; left for 4h before being dried and vacuum dried at 170°C. Finally, the catalyst was treated with 15ml ammonia solution and left to soak overnight. This catalyst (Co-HFC) could thus be compared with the ammoniation series catalyst Co-C24hA.

The CO-HFC catalyst was operated at 39°C with an average propene/propane WHSV of $14,5h^{-1}$. The Co-C24hA catalyst was operated at 40°C with an average WHSV of $12,2h^{-1}$. Plots of conversion against time (Fig. 3.14) indicate that despite a higher WHSV, the LP for the Co-HFC was markedly reduced.

3.4 The Cobalt Hexa-amine Nitrate Complex Catalyst

This catalyst was made to test various hypotheses concerning the nature of the active sites on the double ammoniated catalyst and the function of the ammonia treatments. A successful method was found to synthesize and load the complex $Co(NH_3)_6(NO_3)_3$ onto an activated carbon support (See section 2.1.2). During the loading process, it was observed that ammonia was liberated. This suggested that a definite interaction was taking place between the carbon and the complex.

TG-DTA analysis of the pure complex (Fig. 3.15) showed that the complex decomposed when the furnace temperature was ca. 300°C. Previous calibration of instrument with standards of known boiling points indicated that a lag of ca. 30°C could be expected between the furnace and the sample. Hence a decomposition temperature of ca. 270°C was expected. This supported the idea that the complex could exist on the activated carbon surface. The TG-DTA analysis of the complex catalyst

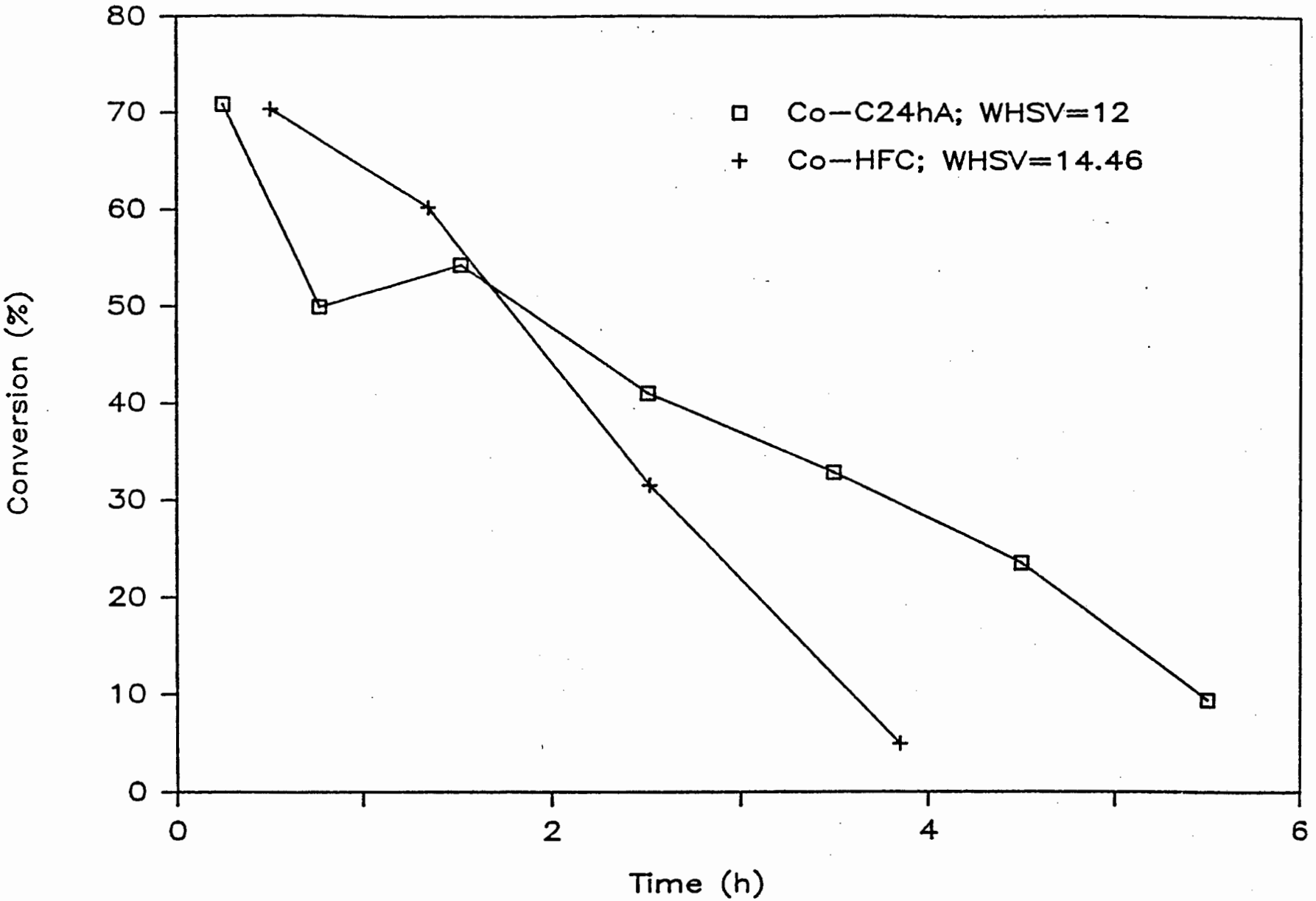


Fig. 3.14: The effect of pretreating the activated carbon with HF.
Catalyst mass = 3g, Pressure = 50 atm, Temp. = 40°C.

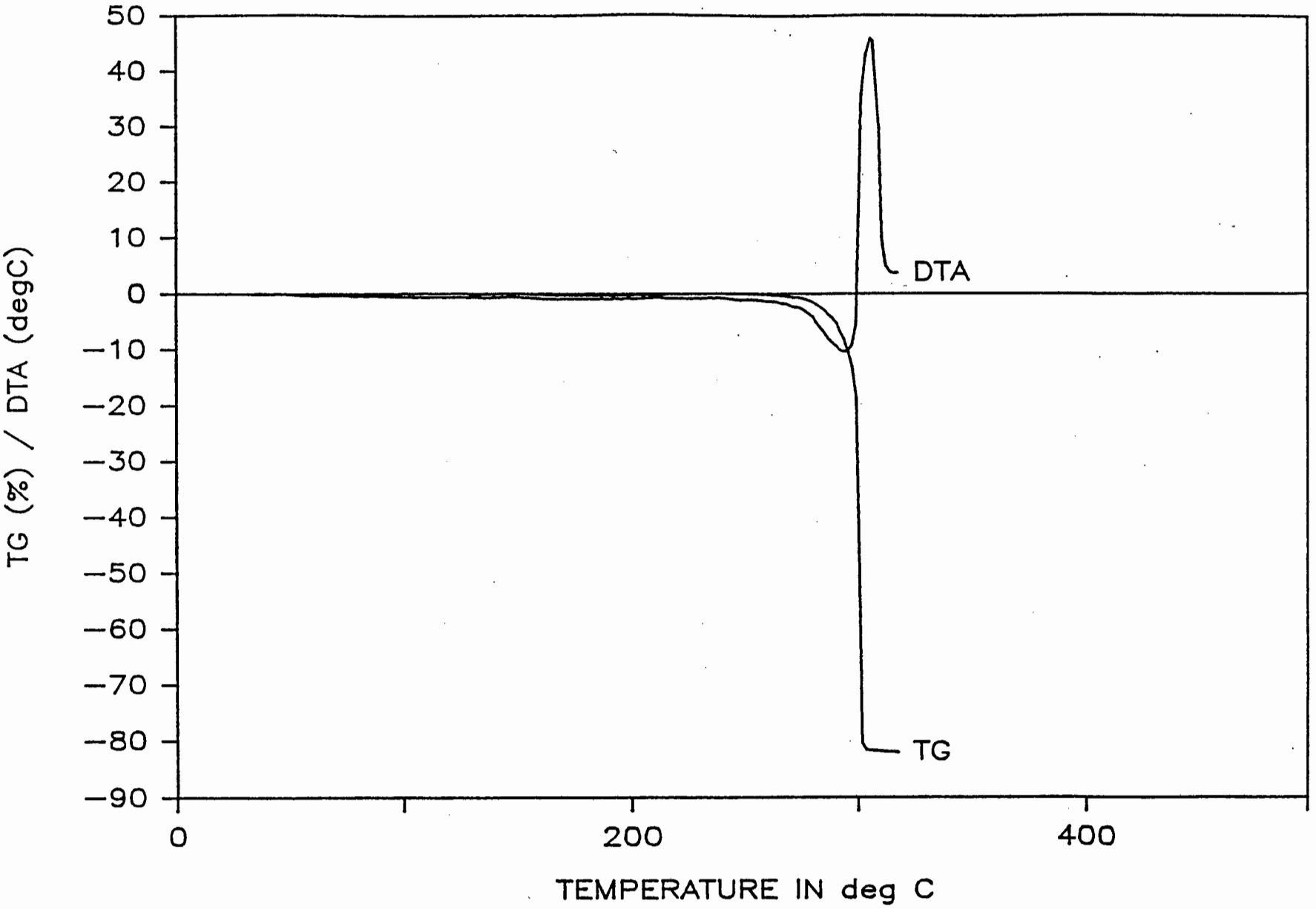


Fig. 3.15: Thermal analysis of $Co(NH_3)_6(NO_3)_3$.

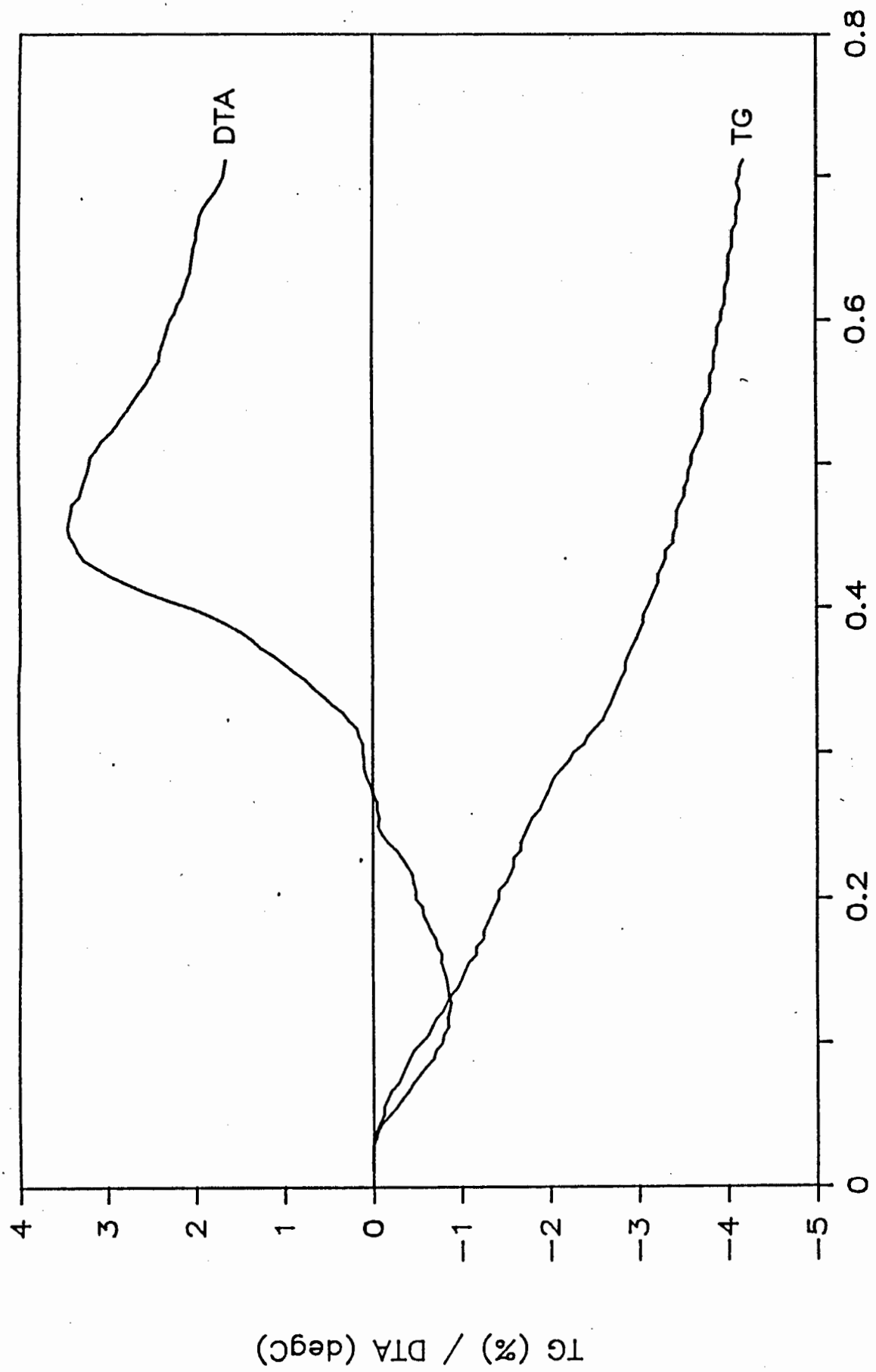


Fig. 3.16: Thermal analysis of Co-Comp catalyst.

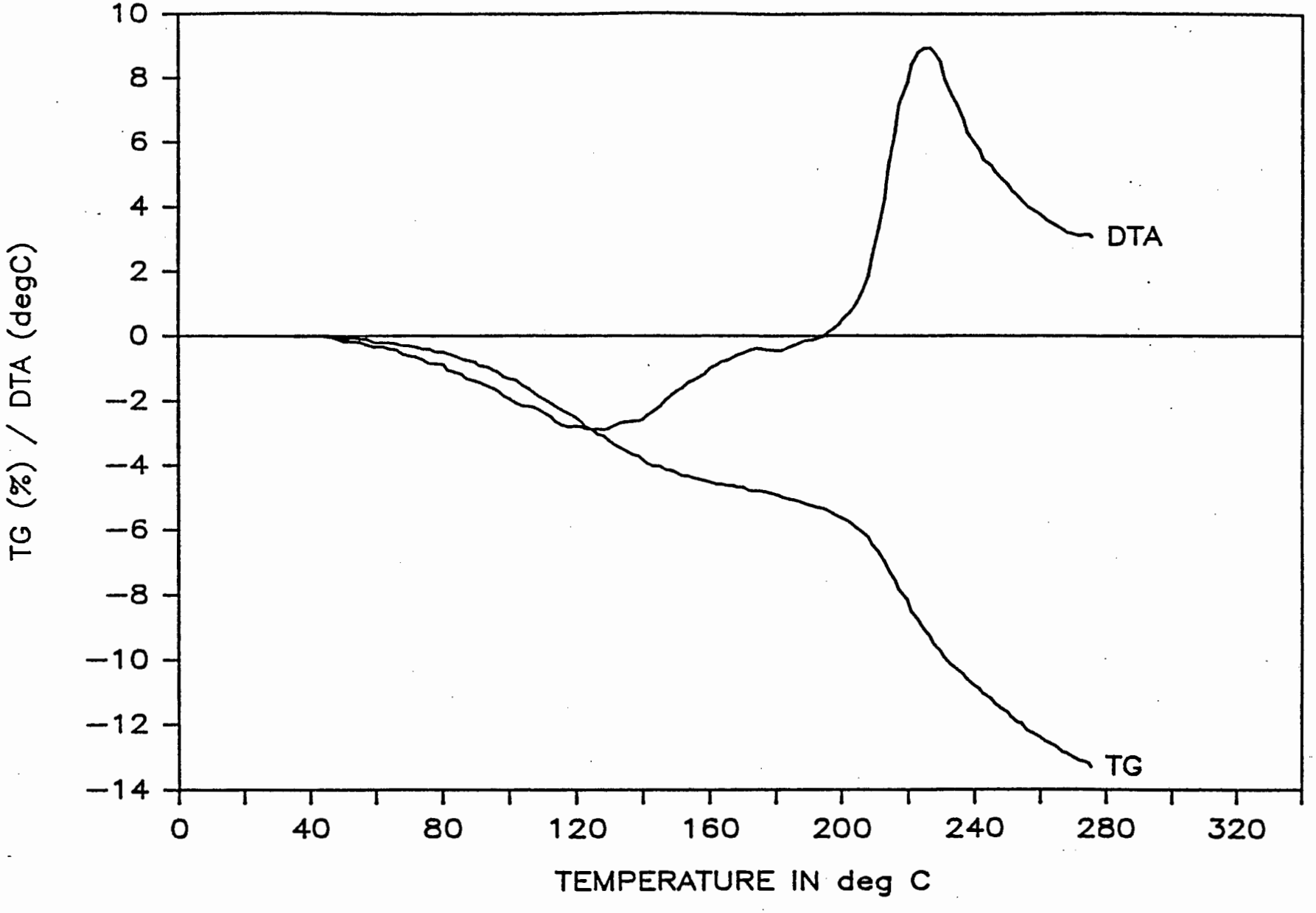


Fig. 3.17: Thermal analysis of Co-C1hA.

(Fig. 3.16) showed similar trends to the double ammoniated version (Fig. 3.17) although the decomposition appeared to be retarded.

To test the hypothesis that the carbon interacting with the complex was active, the catalyst was calcined at 120°C. This was done by heating the catalyst to 120°C over 1,5h and holding that temperature for 1,5h. As usual, a partial vacuum with UHPN_2 bleed of 100ml/min was exerted during the entire calcination. When exposed to the reaction conditions of 50 atm and a WHSV of $6h^{-1}$, no indication of any activity was observed. Temperatures of 25, 65 and 105°C were tested.

A second sample was calcined at 250°C (heated to 250°C over 3h and held at that temperature for 1,5h) under partial vacuum and UHPN_2 bleed. When tested, slight activity was observed at 40°C. Over the first hour, a conversion of 8,4% was obtained at a WHSV of $7,7h^{-1}$. The run lasted 2h and total liquid production of 1,3g/g was measured.

A second batch of complex loaded catalyst was synthesized although now with the modification of a 1h post ammoniation treatment. The calcination was as for a normal double ammoniated catalyst. Negligible activity was observed.

Finally, a sample of the ammoniated complex catalyst was calcined at 300°C for 2h under partial vacuum and UHPN_2 bleed. At a reaction temperature of 40°C, 1g of liquid was produced per gram of catalyst. Clearly, the higher calcination temperature which was intended to ensure more complete decomposition of the complex, did not activate this catalyst.

3.5 Cobalt on τ-Alumina

The 10 wt% Co impregnated catalyst was calcined at 380°C under flowing UHPN_2 for 5h. This treatment was known to decompose the nitrate precursor. Of interest were the crystallites formed. Since τ-alumina possesses no oligomerizing ability, any activity observed would be due

to these crystallites or some Co-Al interaction. The latter was a possibility when considering the Co/Mo-τ-alumia catalyzed metathesis reaction.

The propene/propane feed was passed over the catalyst at 50 atm and 40°C, 75°C, 135°C and 180°C. No activity was observed.

3.6 Cobalt on Silica Alumina

Unlike τ-alumina, silica alumina is an acid catalyst which is known in the literature as an hydrocarbon conversion catalyst. Its activity begins to manifest itself only at ca. 150°C at 50 atm in a fixed bed operation. As discussed previously, NiO on silica alumina is active for oligomerization at 70°C. Silica alumina was thus a good example of a support which exhibits a SMSI which is not obscured by activity of the support.

3.6.1 Control Experiment

The oligomerization reaction was carried out over extrudates of silica alumina powder containing 30 wt% kaolinite. The reaction conditions were 180°C and 50 atm with an average WHSV of $5,3h^{-1}$. Fig. 3.18 shows the data. Analysis of liquid products (Fig. 3.19) showed a significant selectivity to the diesel range. Again, catalyst deactivation was reflected by the shift to lighter products.

3.6.2 Co- Silica Alumina

A first sample of 3,7g of active catalyst was calcined at 380°C under flowing air. As shown in Fig. 3.20, a low conversion was obtained at 70°C and a WHSV of $6,2h^{-1}$. The lifetime was also low. On stepping to 180°C after 4h on stream, a very similar activity to that of the control case was obtained (compared in Fig. 3.18). This suggested that the drop in calcination temperature had not been that significant. Nevertheless, a second sample was calcined at 480°C with no improvement in low

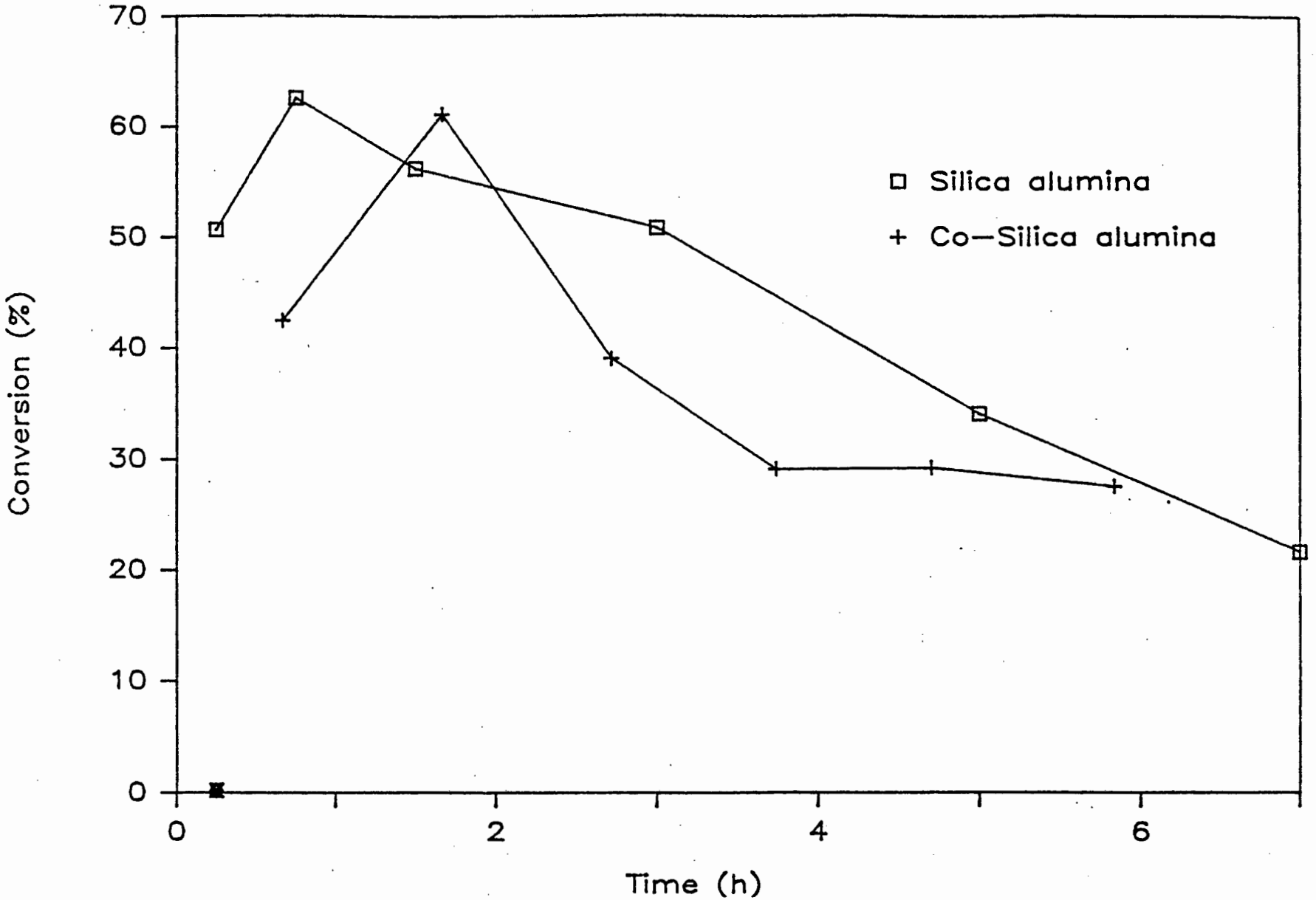


Fig. 3.18: The effect of cobalt impregnation onto silica alumina.
Catalyst = Si/Al (7g), WHSV = 5,3h^{-1}, Pressure = 50 atm, Temp. = 180°C.
Catalyst = Co-Si/Al (3,7g), WHSV = 6,2h^{-1}, Pressure = 50 atm, Temp. = 180°C.

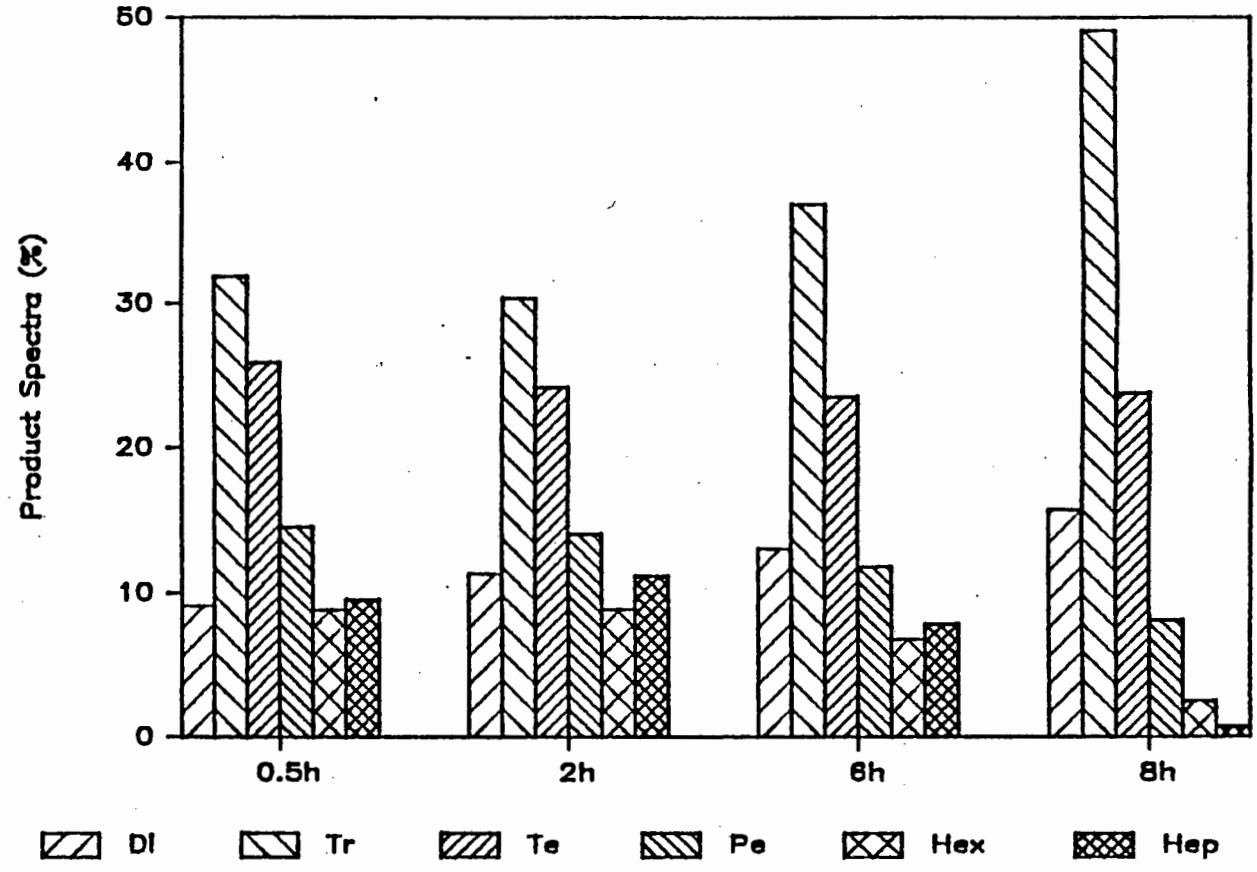


Fig. 3.19: Product spectra of silica alumina as a function of run time. Catalyst = Si/Al, WHSV = 5,3h^{-1}, Pressure = 50 atm, Temp. = 180°C.

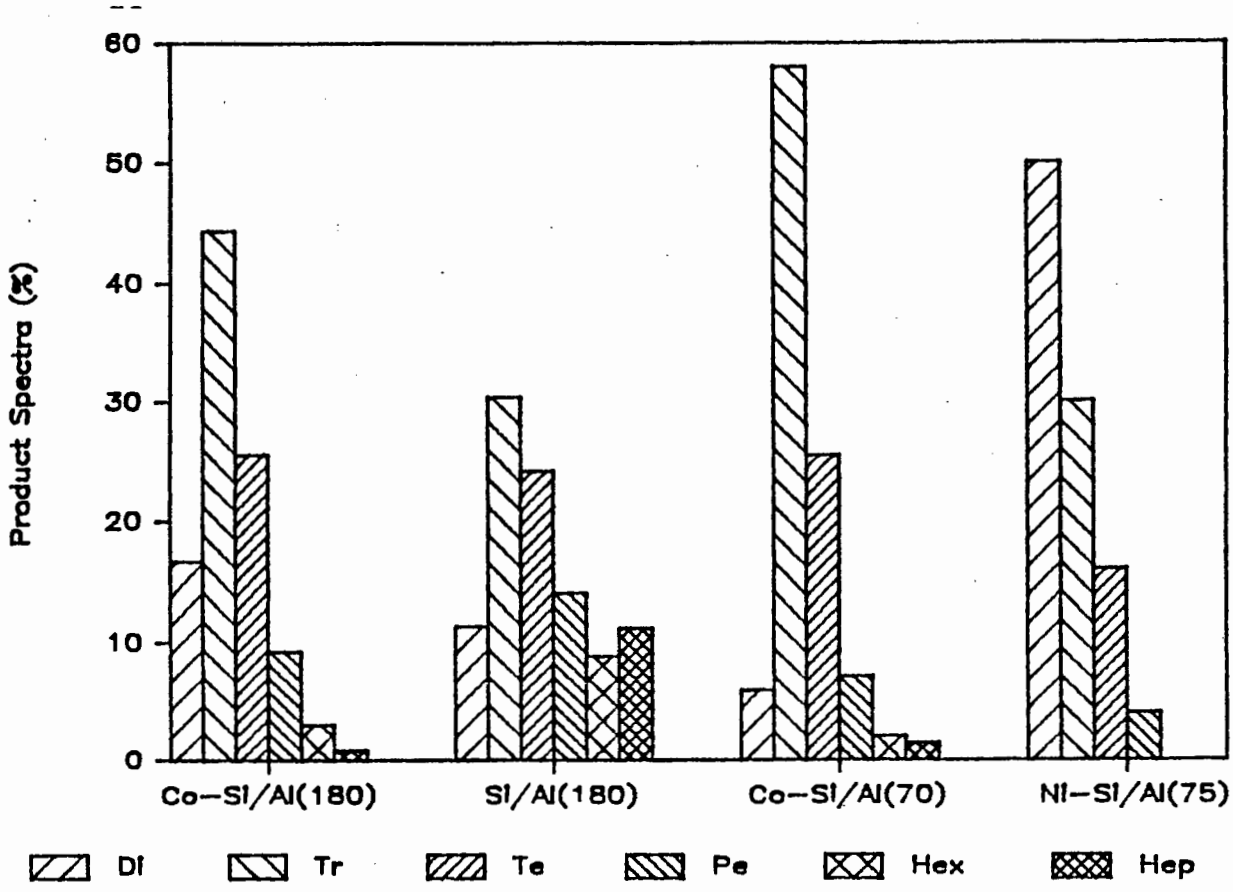


Fig. 3.21: Liquid spectra of cobalt and nickel on silica alumina. (Reaction temperature in parenthesis).

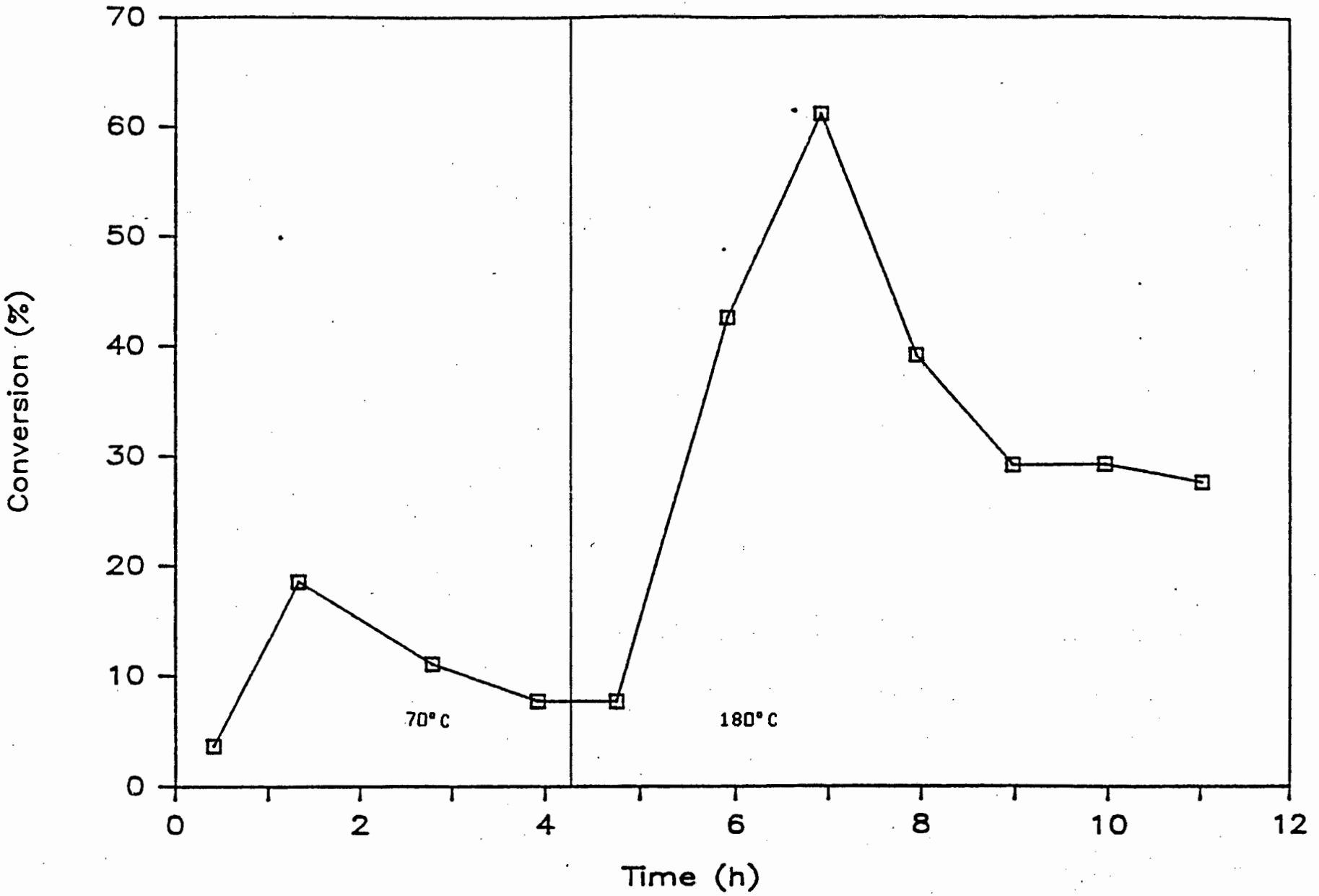


Fig. 3.20: Conversion vs. run time for Co-Si/Al.
Catalyst = Co-Si/Al (3,7g), WHSV = 6,2h^{-1}, Pressure = 50 atm, Temp. = 70°C, 180°C.

temperature conversion. The conversion at 180°C was lower than the control for 2 possible reasons: firstly, it had been on stream for 4h before being tested at the higher temperature; and secondly, the mass of cobalt impregnating salt reduced the mass of silica alumina charged to the reactor. The WHSV effectively increases to $7,4h^{-1}$ taking only silica alumina into account as opposed to the value of $5,3h^{-1}$ for the control. This would naturally lead to a lower conversion. The liquid spectra of the cobalt catalyst for the 70°C reaction temperature showed a large trimer content. This contradicted the spectra obtained for a Ni-silica alumina catalyst (Fig. 3.21). The nickel catalyst is largely a dimerising catalyst.

3.6.3 Co/Mo-Silica Alumina

This commercially supplied hydrodesulphurizing catalyst (5% CoO, 14% MoO_3, 1,2% SiO_2) was of interest because it had both acidity and a metathesis function. 3g of this catalyst was calcined at 470°C for 7h in flowing air. Since it was not known under what conditions (if any) the catalyst would be active, the bed temperature was raised through 4 values - 70 (2h), 140 (2h), 160 (2h) and 200°C (4h). The pressure was held at 30 atm for comparison with the literature of non acidic supported metathesis catalysts. Table 3.4 shows the results:

TABLE 3.4: Metathesis run data.

Sample	Temp.(°C)	WHSV(h^{-1})	Conversion(%)	R	Error
1	68	14	-	-	-
2	140	12,4	10,4	0,831	9%
3	160	12,2	9,69	0,827	8%
4	200	9	8,4	0,829	8,6%

In Table 3.4, the conversion was the mass percent propene converted; R was the mole ratio of the sum of butenes to ethene in the flue gas; the error was the percentage difference between the mass of propene lost and

the mass gain of ethene and butenes. The error was the result of hydrocarbon accumulating on the catalyst, from experimental error in analysis and the usual unavoidable leaks for the high pressure rig. The distribution of mass percents of the gases were as follows, sample 1 being the feed:

TABLE 3.5: Metathesis Products

Time(h)	Propane	Propene	Ethene	N-Butene	c2-Butene	t2-Butene
1	15,1	84,8	0,15	-	-	-
4	14,8	76,3	3,4	0,07	3,2	2,3
5,5	14,8	76,6	3,3	0,10	3,0	2,3
6,5	14,8	77,7	2,8	0,08	2,7	2,0

A clear metathesis function was observed but no liquid product was obtained. It was clear that the catalyst deactivated during the course of a run. It was surprising that the R value did not diminish with increasing temperature: the C_4's would have a higher tendency to polymerise and form coke than ethene. The low formation of n-butene and the high formation of cis- and trans-butene was in agreement with the heats of formation of the C_4 isomers and the reaction mechanism (Fig. 1.7).

3.7 Cobalt Supported on SMM

3.7.1 Control Experiment

Protonated SMM is known to oligomerise propene. This section describes the control experiment necessary to observe any synergistic effects of a low percentage ion-exchange. Since the lifetime of SMM at 130°C and a WHSV of $8h^{-1}$ has been reported to be over 24h and product spectra are not a strong function of time on stream (Jacobs, 1987), it was considered to be reasonable to test both 70°C and 130°C during the same run.

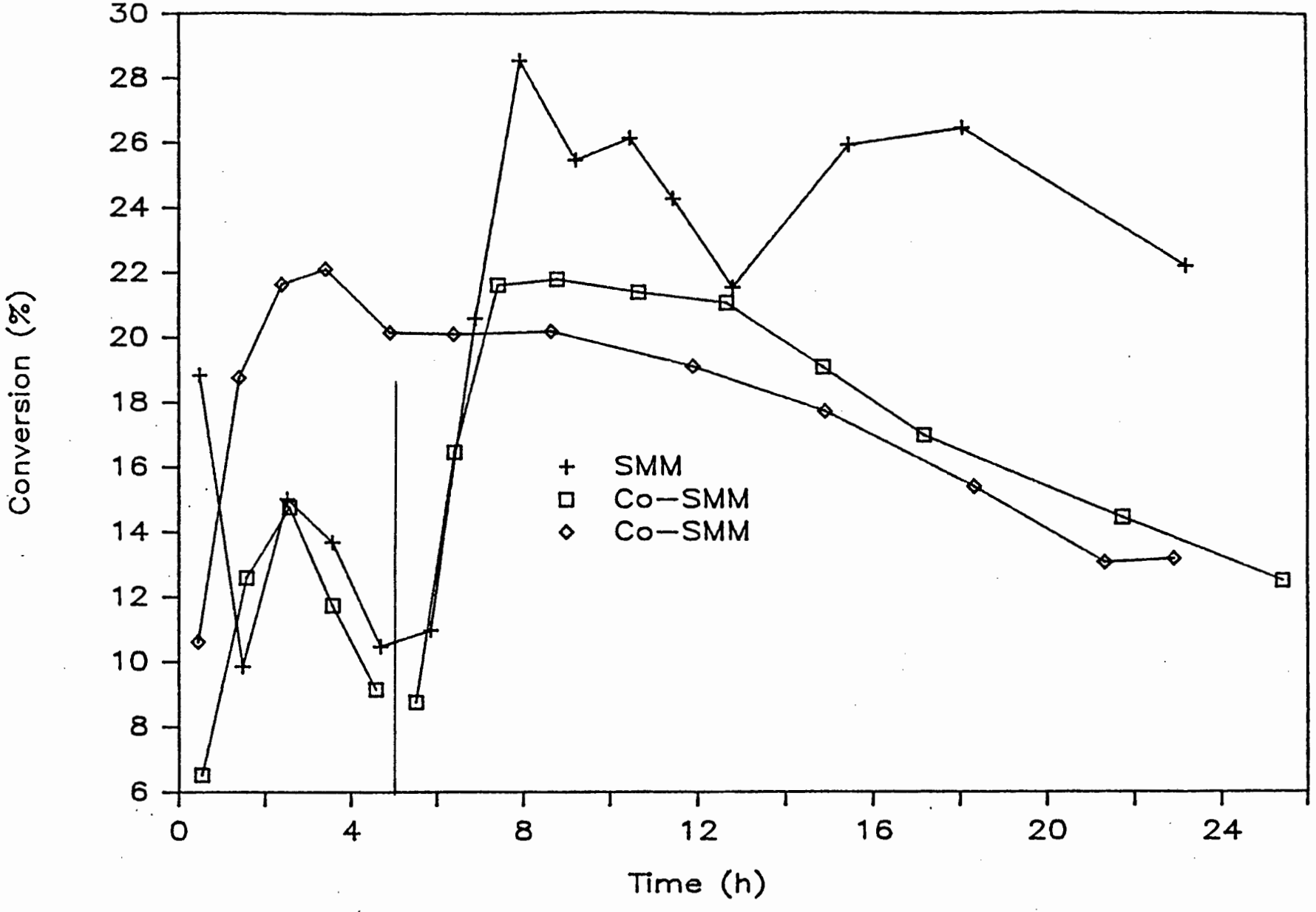


Fig. 3.22: The performance of the SMM catalysts.
Catalyst mass = 3.0g, WHSV = 8.5±1h^{-1}, Pressure = 50 atm, Temp. = 70°C, 130°C.

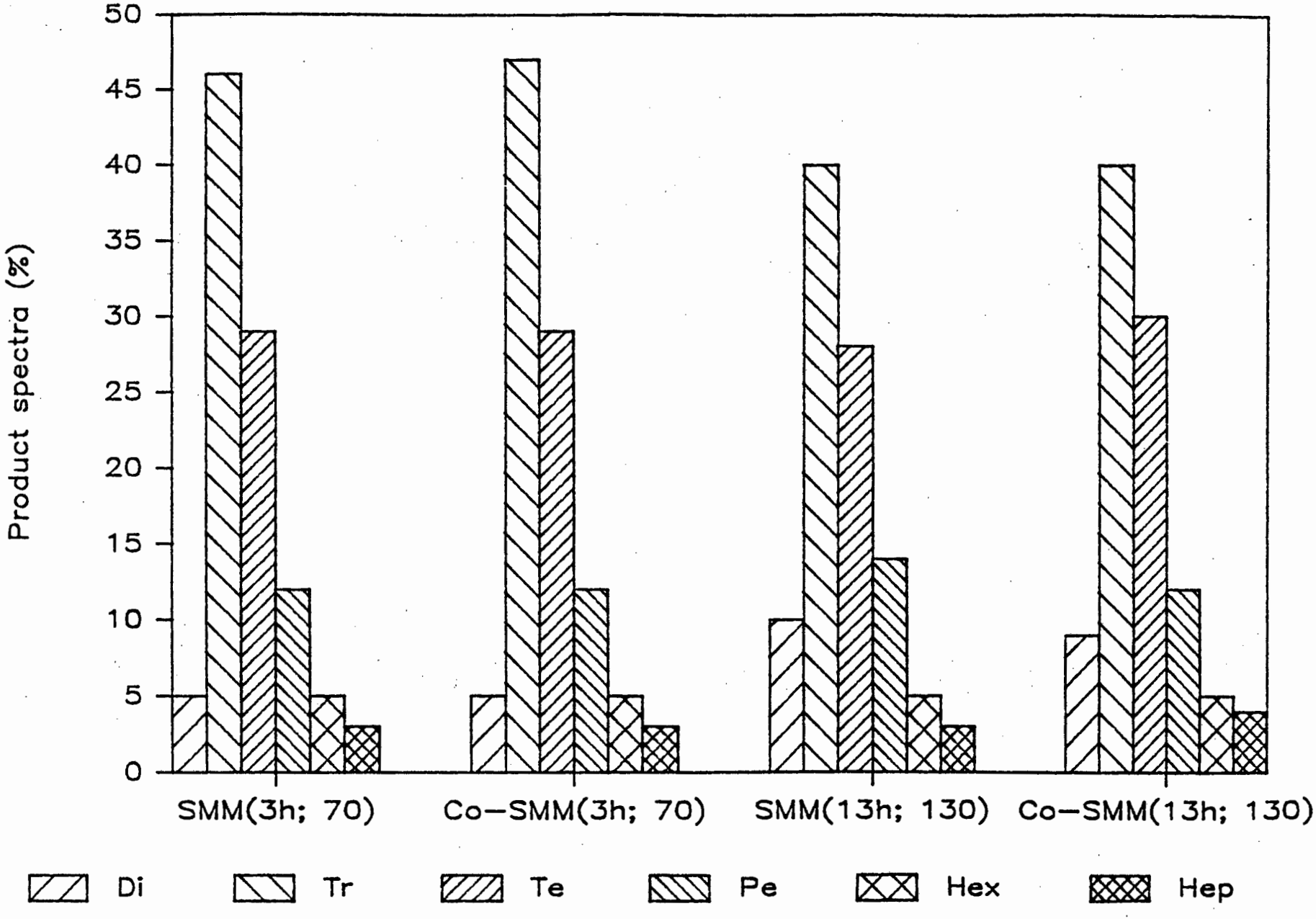


Fig. 3.23: Liquid spectra for the SMM catalysts.
WHSV = 8,5±1h^{-1}, Pressure = 50 atm.

3g SMM was packed and calcined at 470°C in flowing UHPN_2 for 4h. Both the production of liquid and the lifetime were low at 70°C (Fig. 3.22). Increasing the temperature to 130°C gave the values reported previously (Jacobs, 1987). Irregularities in the conversion curve were the result of fluctuations in the WHSV. Liquid analysis is discussed below.

3.7.2 Co-SMM

Two runs were undertaken: the first had virtually identical temperature/time operating conditions to that of the control; the second was started up immediately at the higher reaction temperature of 130°C. The two ion-exchanged catalysts show a very good reproducibility (Fig. 3.22). The the 4h reaction at 70°C did not significantly affect the conversion at the increased temperature. This suggested that the deactivation at 70°C was the result of adsorbed product which was blocking sites. The increased temperature would help desorb these hydrocarbons. The increased conversion at 130°C would also be attributed to a change in mechanism with changing phase (from liquid to gas phase) and simply the faster reaction kinetics. Conversion of the ion-exchanged catalyst was significantly lower than the raw support. Product spectra at both 70°C and 130°C were largely unaffected by the introduction of cobalt (see Fig. 3.23).

3.8 Cobalt on Zeolite Y

In trying to obtain a control experiment, protonated zeolite Y powder (LZY 82-P) gave temperature runaways on startup. The catalyst was totally deactivated by these runaways. $^1/_{16}$" pellets were less reactive. A maximun temperature runaway of 22°C above ambient was experienced. When tested at 145°C with a WHSV of 2,5h^{-1} and a pressure of 50 atm, 1,8g of liquid was produced per gram of catalyst over 5h. Conversion decreased from 24,7% to 6% over this period. A typical liquid analysis was 8% dimer, 35% trimer, 28% tetramer, 13% pentamer, 7% hexamer and 9% heptamer.

The catalyst (Co-LZY52) made by ion exchanging 41,8% of the Na content of LZY52 $^{1}/_{8}$" pellets was calcined at 380°C for 6h in $UHPN_2$. No low temperature activity was observed. A conversion of 15% was obtained at a temperature of 180°C and a WHSV of $6h^{-1}$ although it dropped rapidly to 10% within 1h. Temperature increases to 250°C did not lead to renewed activity. A typical liquid product was 6% dimer, 58% trimer, 26% tetramer, 7% pentamer, 2% hexamer and 2% heptamer.

A sample of the cobalt exchanged LZY52 was soaked in ammonia solution. It was calcined in the same procedure as for Co-C catalysts ie. 260°C, a partial vacuum of 3mmHg and a $UHPN_2$ bleed of 120ml/min. The duration of calcination was 4h. A low activity was observed at 88°C when testing this catalyst. At a WHSV of $6,5h^{-1}$, 3g of catalyst gave an initial conversion of 23,5% with the value dropping to 9% over 4,5h. Liquid spectra were typically 7% dimer, 34% trimer, 35% tetramer, 14% pentamer, 7% hexamer and 3% heptamer. Increasing the temperature to 130°C did not reactivate the catalyst.

3.9 Cobalt on NH_4^+-ZSM-5

3.9.1 Control Experiment

As discussed in section 2.1.7, a batch of NH_4^+-ZSM-5 was synthesized. A sample of this batch was used for the control experiment and the remainder was impregnated with 4,5 wt% Co. The latter was washed thoroughly to give a 1,1 wt% Co loading assumed to be ion exchanged.

3g of NH_4^+-ZSM-5 was packed and calcined at 470°C for 26h. When passing propene over the catalyst, no activity was observed below 180°C. The conversion/run time plot is shown in Fig. 3.24. Again, the reaction temperature was stepped up during the same run to gain a fuller picture of the catalyst activity. Despite a WHSV of over $6h^{-1}$, very high conversions were obtained at 280°C and 330°C. At these temperatures, the liquid product became a yellow colour with a fluorescent green tinge.

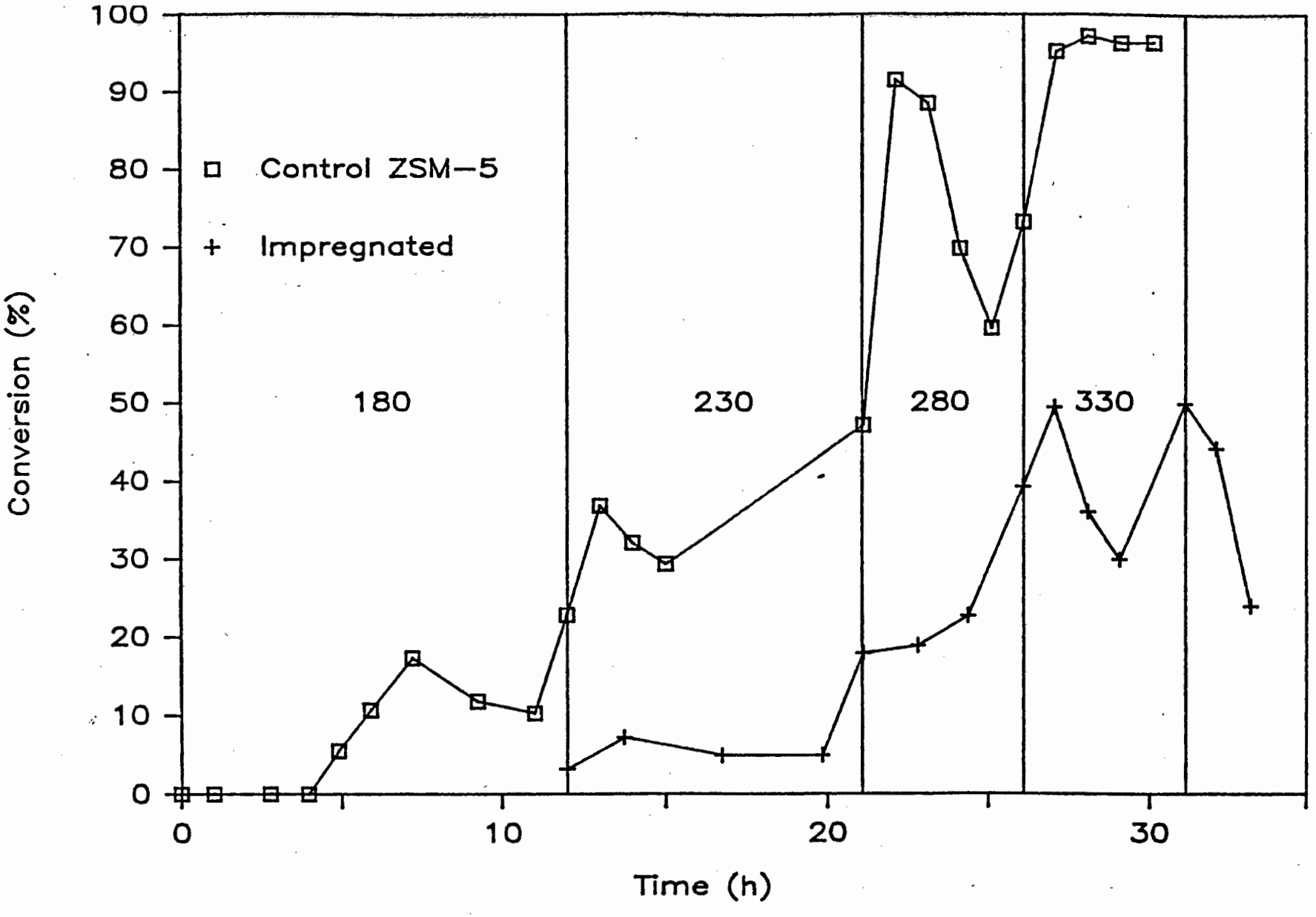


Fig. 3.24: The effect of cobalt impregnated on NH_4^+-ZSM-5.
Catalyst mass = 3g, WHSV = 6,0±0,5h^{-1}, Pressure = 50 atm.

The colour reduced in intensity with deactivation. Product specta are tabulated in Table 3.6:

TABLE 3.6:

Time(h)	Temp(°C)	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
6	180	9	46	28	11	4	2
8,5	180	7	44	28	12	5	4
11,5	230	12	37	24	12	6	8
12,5	230	16	46	26	9	2	1
15,5	280	30	38	25	7	1	0,3
17,5	280	17	32	26	11	7	8
21,5	330	25	32	24	9	4	5
22,5	330	25	32	24	9	4	6

3.9.2 Cobalt Impregnated NH_4^+-ZSM-5

Fig. 24 shows the result of an experiment done with 3g of this catalyst. It is important to note that some data sets have been shifted on the time scale to fit the temperature ranges shown in the figure (true times can be seen in Fig. 3.25). The impregnated catalyst was calcined in the same procedure as the control. The catalyst only became active at 230°C as opposed to the 180°C for the control and the activity was reduced. The zero data points indicate no activity as temperature was raised from ambient. A significant factor here was the fact that the Co analysis of 4,5 wt% could imply that as much as 0,656g of the 3g of packed catalyst could be $Co(NO_3)_2 \cdot 6h_2O$. Hence only 2,34g of NH_4^+-ZSM-5 was packed. This made comparison between the two runs difficult. If the run data was normalised to 2,34g of catalyst, then both the WHSV and the rate of liquid production would go up although the conversion would remain unchanged. LP data for both runs are plotted in Fig. 3.25. It was clear that a significant reduction in activity resulted from this cobalt impregnation. Product specta for the cobalt impregnated catalyst are tabulated in Table 3.7:

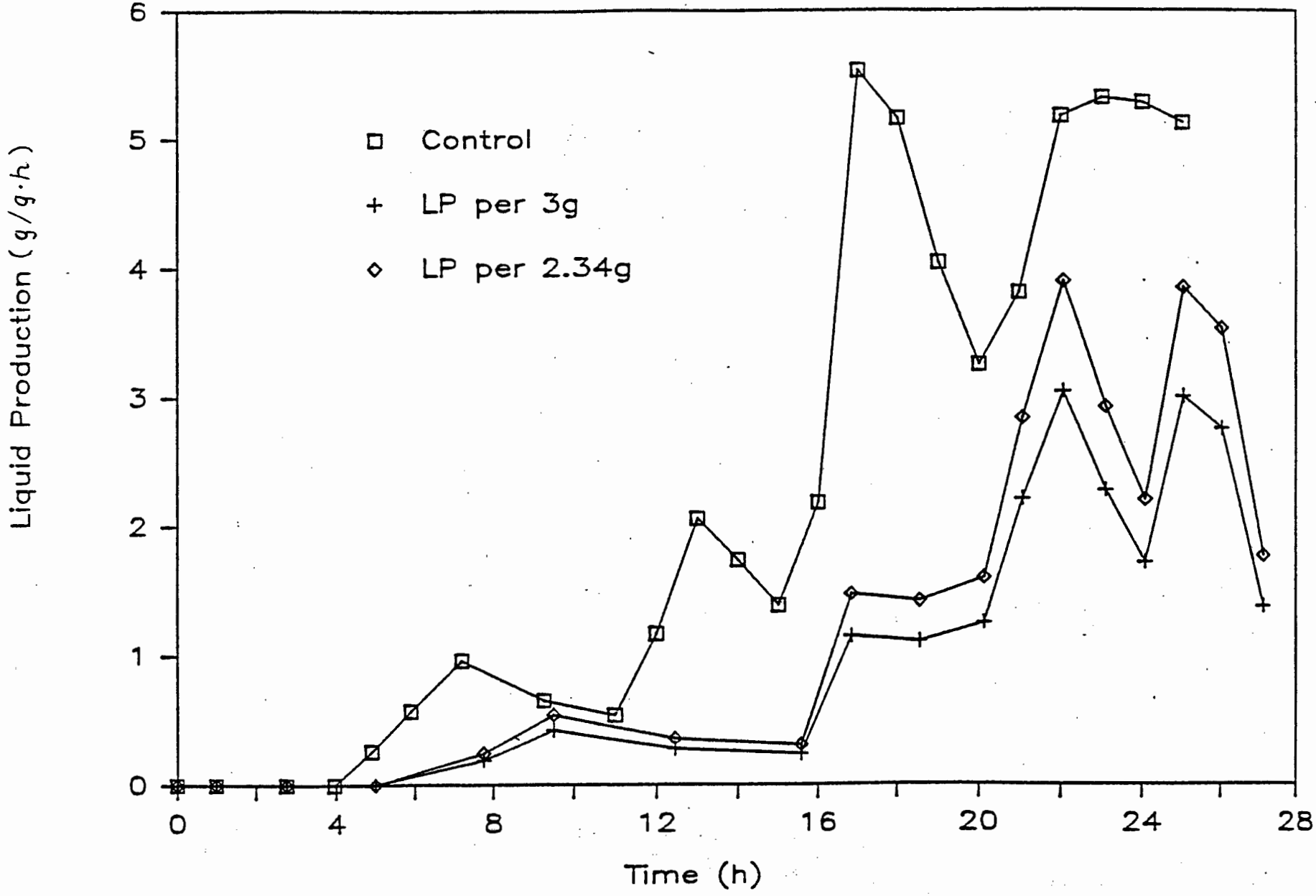


Fig. 3.25: The effect of normalizing cobalt impregnated NH_4^+-ZSM-5 for active mass.

TABLE 3.7 : Liquid spectra for cobalt impregnated NH_4^+-ZSM-5.

Time(h)	Temp(°C)	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
13	230	9	49	30	10	1	1
15,5	280	13	35	24	14	6	8
21,5	330	23	40	26	7	2	1
23,5	380	26	36	23	7	3	4
24,5	380	35	42	19	3	1	0

3.9.3 Cobalt Ion Exchanged NH_4^+-ZSM-5

The weight normalisation problems experienced with the impregnated form were not experienced here as all Co was believed to be ion exchanged. The same temperature steps as for the impregnated catalyst were used here (viz. 30-180, 180, 230, 280, 330°C) and an extra datum of 380°C was also tested. These steps clearly correspond to the conversion increases shown in Fig. 3.26. The activity was again reduced at 180°C. At 230°C, the conversion was fairly similar whilst at 280°C the conversion of NH_4^+-ZSM-5 was significantly higher. The product distribution as a function of reaction temperature is given in Table 3.8:

TABLE 3.8: Liquid spectra for cobalt ion-exchanged NH_4^+-ZSM-5.

Time(h)	Temp(°C)	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
3	230	7	39	26	13	7	7
7,5	280	13	35	27	15	5	5
11	330	12	34	31	16	5	3

3.9.4 A Cracking Index

The liquid composition data shown above did not reveal much although inspection of the chromatograms revealed that cracking became a

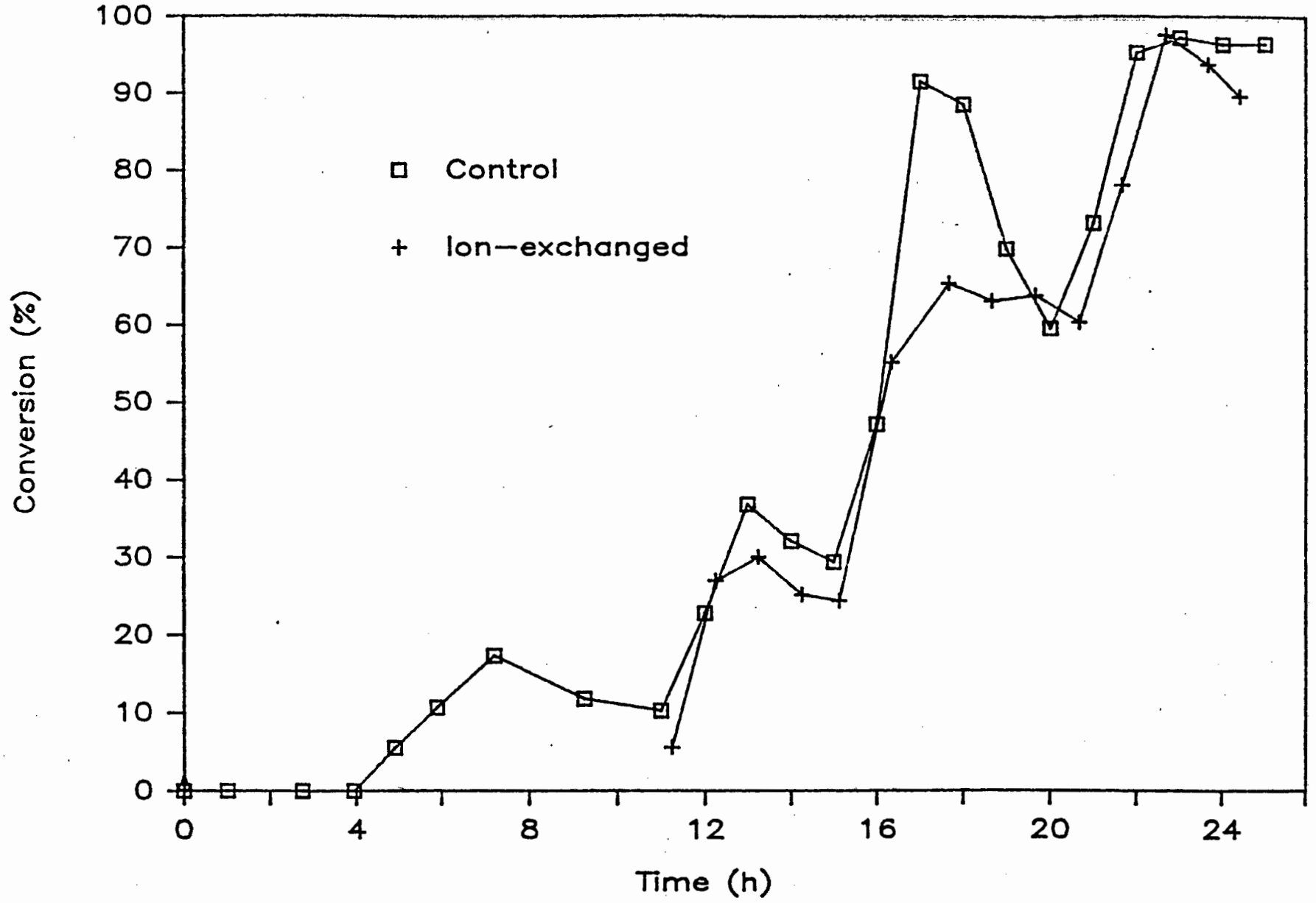


Fig. 3.26: The effect of cobalt ion-exchanged into NH_4^+-ZSM-5.
Catalyst mass = 3g, WHSV = 6.0±0.5h^{-1}, Pressure = 50 atm.

significant factor with increasing temperature. It was relevant to investigate whether cobalt inhibited or promoted this phenomenon. A Cracking Index (CI) was defined to facilitate comparison. In the absence of cracking, only pure oligomers with carbon numbers in multiples of three would be present. The presence of hydrocarbons in the range C_7 and C_8 could only have arisen through cracking. The CI was thus simply defined as the percentage of C_7 and C_8 in the liquid product. Experience showed that a value of 4 indicated low cracking levels whilst a value of 15 was excessive. Data for the above runs are given below:

TABLE 3.9: Cracking Index.

Cracking Index (time on stream (h) at given temp./ conversion(%))			
Temperature(°C)	NH_4^+-ZSM-5	Impregnated	Ion exchanged
180	4,5 (2,5/17)	-	-
	3,7 (4/11)		
230	6,4 (3/37)	4,6 (2,5/5)	5,0 (3/30)
	5,6 (4/32)	4,4 (7,5/5)	
280	15,2 (3/91.5)	6,7 (7/19)	6,4 (5,5/64)
	9,3 (5/70)		
330	14,4 (5/96)	13,2 (3/49)	10 (4/94)
	14,5 (6/96)	10,2 (4/36)	
380	-	19,7 (3/44)	-

Basic trends were an increase in CI with increasing temperature and a decreasing CI with time on stream at a particular temperature. An interesting point arose for the 280°C NH_4^+-ZSM-5 data where the CI fell from 15,2 to 9,3. This drop was associated with a drop in conversion for 91,5% to 69,75%. This leads one to believe that the initial high difference in conversion was accompanied by significant cracking levels. itt may be argued that the sites causing cracking coked rapidly giving

the drop in conversion and CI value. By contrast, the CI values for the cobalt catalysts remained low. This implied that either the number of acid sites which caused the cracking were reduced by ion-exchange or the presence of cobalt reduced cracking.

4. DISCUSSION

It was clear from the results of this thesis that the carbon supported catalysts behaved quite differently from the aluminosilicate supported catalysts. As such, the discussion is split into two sections, the first dealing with the cobalt-carbon catalysts and the second dealing with the cobalt-aluminosilicate catalysts. The third and final section of this chapter gives an overview of the role of cobalt as an oligomerising catalyst and presents the conclusions.

4.1 The Cobalt Carbon Catalyst System

The cobalt-carbon catalysts tested were modelled on the double ammoniated version developed by Schultz et al. (1966a). The high liquid productivities and lifetimes reported by them were not reproduced in this work. The validity of the experimental procedures in this work consequently required investigation.

4.1.1 Validity of Results

It was established early on in this work (in agreement with the literature) that the catalyst was extremely sensitive to the presence of oxygen. Fig. 3.3 showed how a calcination with nitrogen containing 4500 ppm of O_2 severely diminished activity. In their work Schultz et al. (1966a) reported that activated catalyst was packed into their reactor under a nitrogen blanket. The in situ calcination procedure used here was considered to be an even safer and more reproducible procedure. The only danger of oxygen contamination occurred during the switch-over from vacuum line to high pressure rig. However, this was always done under flowing $UHPN_2$. In the event of a significant air leak into the reactor whilst calcining, the experiment would automatically be discarded when the same leak resulted in a large hydrocarbon mass loss in the high pressure phase of the experiment.

The reaction start-up procedures were also important. Firstly, the question arises as to whether the feed was adequately dry. In the absence of a suitable detector, an experiment was devised whereby another oxygen/water trap was installed in the low pressure pre-reactor side of the rig. The manganese oxide trap used is reported to be capable of reducing O_2 concentrations in N_2 streams to parts per billion (Mcillurick and Phillips, 1973). It was assumed that its effectiveness would not be diminished by the presence of the hydrocarbons. For this experiment, another oxy-trap was installed on the $UHPN_2$ calcination line. It was clear from Fig. 3.3 that no significant inprovement was obtained by these modifications. Clearly, a reasonable level of decontamination had been achieved by the molecular sieves. The manganese trap was subsequently removed.

The second important aspect of the start-up procedure was to avoid temperature shocks. The cobalt-carbon catalysts were temperature sensitive. Lifetime was markedly reduced by operating at 80°C as opposed to 40°C. The preliminary work showed that undiluted catalysts experienced start-up thermal runaways of 30-40°C. Hence the catalyst was diluted with glass beads and air flow through the external fluidised bed was set to a maximum. The temperature increase was reduced to ca. 15°C above ambient. This set the minimum operating temperature.

Another factor which could have affected the results was feed purity. The only analytical procedure available was G.C. analysis via F.I.D. No peaks other than ethane/ethene, propene and propane were observed. Importantly, gases such as acetylene and conjugated hydrocarbons like butadiene were not present in detectable quantities. After the purification and fractionation processes at SASOL, it was highly unlikely that CO or sulphonated compounds were present in significant quantities. Schultz et al. (1966a) reported that chloroform, water and furfural were "slightly inhibitory" at low concentrations (20-30ppm) whilst piperylene was extemely inhibitory at concentrations as low as 15ppm.

Finally, the question of reproducibility arises. Fig. 3.1 shows two identical experiments with the same catalyst. The reproduciblity was considered to be acceptable. Factors which caused these discrepancies included variations in ambient temperature and WHSV. Ambient temperature varied by as much as 10°C both during an experiment and from day to day. The time taken to thermally stabilise reaction conditions varied according to ambient temperature variations. A high ambient temperature gave a low temperature difference between the reactor and the sand bath and this made temperature stabilization more difficult. Variations in WHSV were the result of the pump delivering different flows at the same setting. These factors made it almost impossible to reproduce identical reaction conditions from experiment to experiment.

Fig. 4.1 shows the possible error bar for the catalyst Co-C1hA discussed in 3.2. This error band was calculated for the worst extremes of all losses in the form of a leak before the reactor, a gas leak after the reactor and a liquid product loss after the reactor. The errors were based on the total mass loss of 8%. It is clear that the basic trend is unaffected by mass loss (assuming that the mass loss was uniform with time). Hence trends such as the reduced conversion due to increased post ammoniation contact time were considered to be real and identifiable.

4.2.2 The Attempts to Reproduce the Results of Schultz et al. (1966a)

Several difficulties arose whilst attempting to compare the present work with that done by Schultz et al. (1966a). Firstly, virtually all their work was undertaken with a 99% pure propene feed. One experiment reported by them had a 50% dilution with propane. The total liquid production was reduced from 606g/g to 89g/g under similar conditions (although termination conditions were not given). It was not clear how the liquid production varied between the two extremes. No reasonable explanation could be found to explain the negative effect of the propane. The feed used here had typically 86 wt% propene and 14 wt% propane although a 99,9% feed was also tested. No reasonable interpolation could be made between the above two feed mixtures.

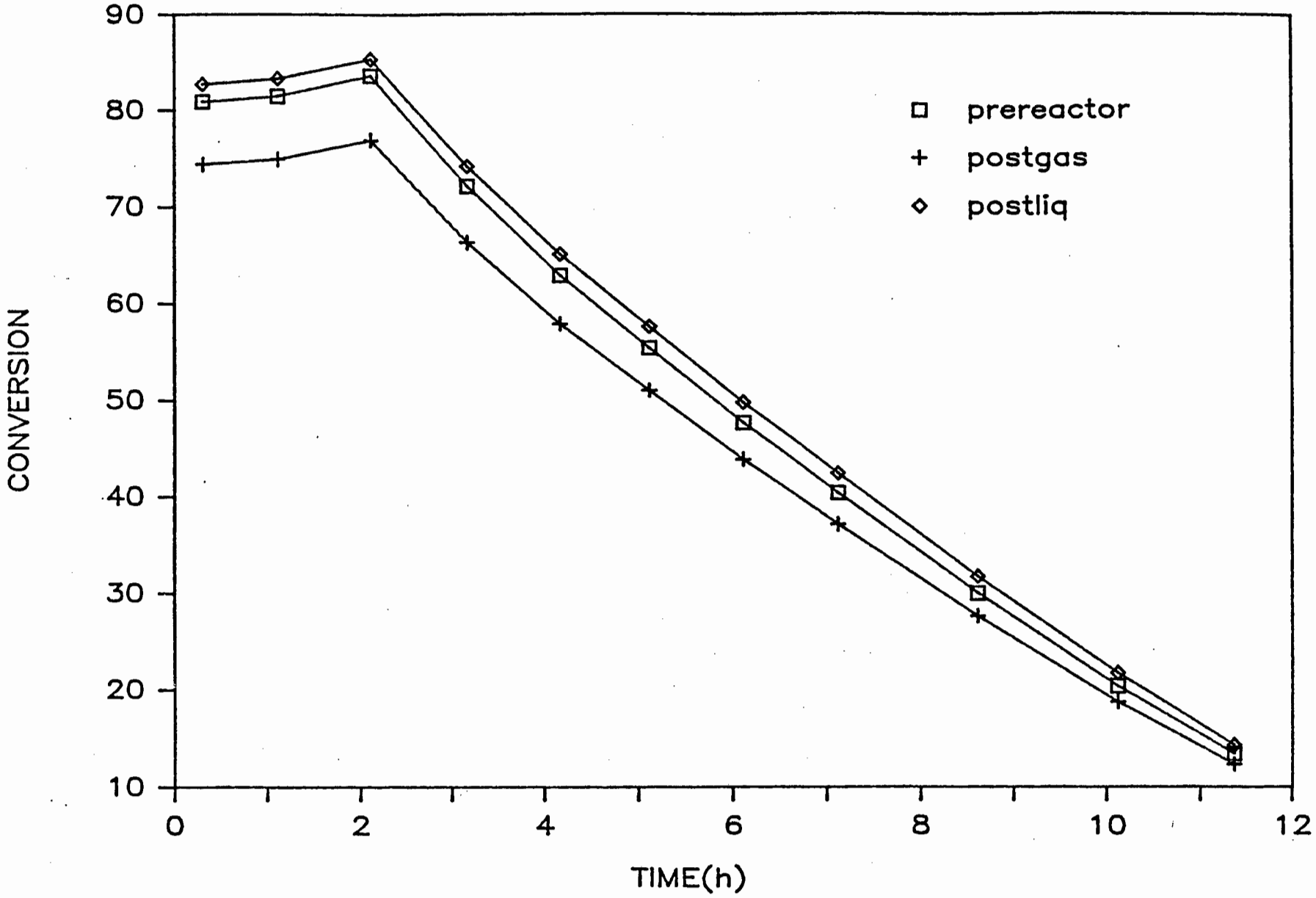


Fig. 4.1: Plot of error bar for worst possible constant mass loss conditions.

Secondly, Schultz et al. (1966a) packed activated catalyst and all their data was presumably normalised to the mass of activated catalyst. The data of the present work was normalised to the mass of fresh catalyst packed. TG-DTA of Co-C1hA showed that 15 wt% was lost when a sample was heated to 275°C over 1,5h and held at that temperature for 1,2h. For comparison between this work and that of Schultz and co-workers, the total liquid production for the Co-C1hA experiment could be recalculated to yield a value of 77g/g as opposed to 66g/g.

Finally, the literature runs by Schultz and co-workers were operated with overall conversions of ca. 9-15% and initial WHSV of ca. 25-33h^{-1}. Operating at these low conversions may have produced higher product yields. In the present work, typical values of overall conversion were ca. 40%. The lack of conversion vs. run time data in the literature also obscured comparison. In one experiment Schuck et al. (1967) report an average overall liquid production of 0,153g/h·g over 736h. It is reasonable to assume that the catalyst deactivated with time and hence the production near the end of the run must have been well below 0,15g/g·h. This is perhaps reasonable with 9g of catalyst but the hourly liquid production becomes almost immeasureable when 1,5g of catalyst is packed. The shut-down criteria for their runs was not stated. Bearing these factors in mind, the ensuing paragraphs outline the variables tested to improve the first synthesis attempt of a double ammoniated catalyst.

It is of interest to compare firstly the simple impregnated catalysts without ammonia treatments. Schultz et al. (1966a) reported a total liquid production of 4,3g/g with an overall conversion of 3% and an average WHSV of 23,2h^{-1}. As described in 3.1.2, the present non-ammoniated catalyst produced 0,56g/g at an average WHSV of 2,2h^{-1}. Conversion for the first 21 min was ca. 55%. The extent to which the activity of this catalyst might be described as being lower than the literature was uncertain. Nevertheless, this simple combination was

active and the synergistic effect of the ammoniation treatments was clear.

The base case (3.1.3) was a double ammoniated catalyst tested at 70°C and 50 atm with an average WHSV of 2,7h^{-1}. The apparent steady state as indicated by the plateau in the conversion figure (Fig. 3.1) was misleading. Traces of temperature vs. time showed a clear reaction front progressing through the undiluted catalyst bed. When the mass of catalyst packed was reduced from 9 to 3 or 1,5g in later runs, no steady state was observed. This was consistent with all the cobalt-carbon catalysts tested. This catalyst deactivation was also implicitly present in the data reported by Schultz and co-workers where the WHSV was varied over a wide range to maintain a particular conversion. The total liquid production of 9,4g/g was insignificant compared to the value of 215g/g reported in the literature for similar conditions. To improve this value, several variables were tested.

Firstly, the temperature was lowered to 40-50°C and at least a 3,5 fold improvement in activity was observed. This result clearly indicated the sensitivity of the catalyst to temperature and it was clear that the reaction temperature should be maintained as low as possible. In fact the question arose as to whether the catalyst should be tested at 0°C. This option was rejected because of the practical problems of converting the fluidised bed into an ice bath and because it was felt that desorption from both the active sites and the usual adsorption sites on activated carbon would be severely retarded at this low temperature.

The possibility that an excess of ammonia was necessary during synthesis, was explored. The preliminary work showed that an increase in activity occurred when the pre-ammoniated activated carbon was dried at 70°C and the post-ammoniated catalyst was left to soak overnight in ammonia and experience evaporative drying. This effect was tested concurrently with temperature reductions and some confusion arose as to which effect caused the improvement in liquid production. The fact that a catalyst synthesized with a zero time post-ammoniation was inactive further suggested that the activity was enhanced by soaking time. Thus

other tests were done with the overnight soak. The ammoniation series work subsequently suggested that a 1h soak in ammonia solution was nearly optimal. Schultz et al. (1966a) gave no indication as to what soaking time was used in their synthesis procedure. They did not suggest that the period of post-ammoniation contact time was an important variable for their catalyst.

Common to all of the literature on Co-C catalysts was the use of (or suggested use of) nitric acid as a pretreatment for the activated carbon. A catalyst was made whereby a nitric acid pretreatment replaced the pre-ammoniation treatment. Simultaneously, an initial high WHSV was tested to imitate the above discussed strategy of Schultz et al. (1966a). Fig. 3.7 shows the results. Either the high WHSV did not improve the total liquid production or the nitric acid pretreatment without pre-ammoniation was detrimental. The latter was more likely since the literature suggested that a high WHSV was beneficial.

By the end of the preliminary work, it was apparent that the ammoniated catalyst had not successfully been synthesized. However, it was clear that the post-ammoniation contact time was an important variable. The other possible explanation for the low activity was that the nature of the activated carbon was not the same as that of Schultz et al. (1966a).

4.1.3 Variation of Post-Ammoniation Contact Time

It was clear from the set of experiments done to test this variable that the period of post-ammoniation was crucial (3.2). The conversion plots show that both initial activity and rate of deactivation are affected by this variable. The table of total liquid productions (Table 3.2) also indicates the strong dependence of conversion on this variable. The difference in liquid production between the ½h and 1h treatments was an increase of 40%.

This variation in activity could explain the disparities in the literature batch reaction data presented in section 1.2.2. Experiments were grouped to illustrate the effect of a particular variable. Often

disparities arose between identical experiments in different data sets. It is possible that irregular contact periods were used. The question also arises as to how the performance of Co-C1hA compares with those reported in the literature. Recalling the problems outlined above, the most comparable datum (Schuck et at., 1967) in the literature would be that of a 50% propane diluted feed. With an average conversion of 16,5% and an average liquid production of 1,89g/h•g, the total liquid produced was 88,9g/g. If the data for Co-C1hA are scaled up for the 15 wt% loss due to calcination, then the experimental data are: an average WHSV of 15,4h^{-1}, an average conversion of 46% and an average liquid production of 6,4g/h•g. The run was terminated when the conversion fell to 13,4%. The main difference between the runs (apart from the propane dilutions) was the fact that a high initial WHSV would have been used in the literature run compared to the WHSV variation in the present run of 0,5h^{-1}.

To test the effect of propane diluent, a 99,9% pure propene feed was used instead of the SASOL feed stream. As seen in Fig. 3.8, no major improvement was observed with this feed modification. The catalyst in this experiment was also calcined at 275°C as opposed fo 250°C. As shown by Fig. 1.1, this calcination temperature should have been more optimal than 250°C. Clearly, both modifications did not require further investigation. The results of this experiment contradicts the drop in liquid production reported by Schultz et al. (1966a) for their 50% propane diluted experiment. The reduction in liquid production may have been due to an early run termination.

The exact liquid spectra were not given by Schultz et al. (1966a) for each of their experiments although they suggested that typically a 95% selectivity to dimer was achieved. This work produced an 80-85% selectivity. This lower selectivity could have been the result of a lower WHSV. It follows from TG-DTA data (Fig. 3.8) that one contributing factor to deactivation was the coking by longer chain hydrocarbons. It is possible that at higher WHSV, the heavier fraction could be reduced especially if the reaction mechanism was one where the dimer competed with the monomer for readsorption and further oligomerisation. However,

since the product spectrum did not shift as the catalyst deactivated, it was felt that the product was not that strongly a function of WHSV. It was therefore possible that the catalyst Co-C1hA had active sites which were different to those of the catalyst synthesized by Schultz et al. (1966a). The catalyst produced a heavier product (18 wt% trimer+ as opposed to 5 wt% reported by Schultz et al. (1966a)) which in turn resulted in a higher deactivation rate.

4.1.4 Hypotheses concerning the Role of Activation Procedures

Firstly, the role of ammonia in a pretreatment of the activated carbon is considered. As outlined in 1.3.3, the adsorption of salts by activated carbon is promoted by the presence of oxygen functional groups. These sites (such as carboxylic acid groups) become negatively charged in basic solutions and are ideal for chemisorbing cations. These carboxylic groups are formed both by the activation procedure of the activated carbon and by the partial oxidation of the surface with reagents such as nitric acid. The ammonia pretreatment is believed to create the basic environment necessary to improve cobalt chemisorption onto the activated carbon. This would improve the dispersion of the impregnated catalyst.

This theory was supported by the batch reaction data reported in the literature and described in 1.2.2.2. In these experiments the activated carbon was washed with nitric acid, then base and finally impregnated with $Co(NO_3)_2$. Where no base treatment was undertaken, the liquid production was 3,3g/g. The ammoniated analogue had a four-fold improvement to 13,8g/g. The data showed that different bases gave different results. For instance, pyridine gave a yield of 8g/g. Clearly, the ammonium ion was not essential for improved activity in the pretreatment phase. The NaOH treated catalyst was hardly activated. It is believed that these Na^+ ions prevented ion exchange of the cobalt onto the activated carbon.

If it is true that the function of the ammonia pretreatment is primarily to improve dispersion via oxygen functional groups, then two points

emerge. The first is that improved interaction between the cobalt and the oxygen functional groups improves catalyst activity. Secondly, the promoted activity is due either to an essential cobalt-oxygen functional group interaction or high levels of dispersion.

As mentioned in the results (3.2), a strange observation made during the synthesis of the ammoniation series of catalysts was that Co-C½hA had a milky blue coloured external surface whilst the rest of the series were black. This blue colour was reminiscent of $Co(OH)_2$ or ammoniated cobalt(II) compounds. In the absence of suface analysis techniques, the following speculations are made as to the role of ammonia in the post-ammoniation treatment based on this and other observations. The first hypothesis is concerned with the dispersion of cobalt whilst the second proposes a dynamic site (or site precursor) theory.

Once the nitrate salt has been impregnated and the catalyst dried, it is envisaged that crystallites of $Co(NO_3)_2$ and CoO_x exist throughout the pores. It is possible that the low activity of the non-ammoniated catalyst could be due to poor dispersion. The addition of aqueous ammonia results in a vigorous exothermic behaviour. This could be due to heat of adsorption onto the activated carbon, heat of co-ordination of the ammine complexing with the Co^{2+} ions and some heat of reaction of any nitrate being converted to the hydroxide. As shown by the cell potentials in Table 1.7, the ammonia co-ordinated ions are far more stable than the hydrated ions. Due to the vigorous nature of the reaction, the cobalt is believed to be driven out of the pores and onto the outer surface of the activated carbon. This is in accordance with the observed blue cobalt salts located on the surface of the ½h post-ammoniated catalyst.

When left for several hours in a wet state, it is conceivable that the salts progressively diffuse back into the pores of the activated carbon. Rapid drying ends further migration of salts. The lower initial activity and total liquid production of the long exposed catalyst (Co-C24hA) could be due to migration of cobalt into inaccessible pores.

Alternatively, it is possible that an active site (or active site precursor) is slowly formed by the ammonia addition in the post-ammoniation step but subsequently decomposes with time. The carbon catalyzed formation of Co(III) hexaammine nitrate (1.3.3.1) is an example of gradually forming species. The reaction is :

$$4Co(II)(NO_3)_2 + 4NH_4NO_3 + 20NH_3 + O_2 = Co(III)(NH_3)_6(NO_3)_3 + 2H_2O.$$

Although not added in the synthesis, the ammonium nitrate could be present due to the reaction of cobalt nitrate with ammonium hydroxide (present in the ammonia solution). Clearly, the ammonium nitrate simply provides ligands for the complex. In the presence of the activated carbon, the charge balancing role of the nitrate ligands could be assumed by oxygen functional groups. It is also known that the above reaction takes time to come to equilibrium. Bjerrum and McReynolds (1946) suggest that 4h is sufficient for the reaction to reach equilibrium although in the present study it was observed that a significant conversion takes place within the first hour. This was judged purely by observing the crystal formation during the synthesis. Further, $[Co(NH_3)_6]^{3+}$ eqilibrates with time to give $[Co(NH_3)_5(OH)]^{2+}$ (1.3.3.1) in the presence of an activated carbon catalyst.

An important factor supporting this theory of a dynamic site was that a catalyst given an "instantaneously" post-ammoniation treatment gave almost no activity. It is possible that the active site could be some combination of Co(II) and Co(III) ions co-ordinated with any number of hydroxy and amine groups. The number of sites could be affected by the extents of the various reactions, ie., is a function of time.

It must be pointed out that in the event of the activated carbon already having a fully oxidised surface, no further oxidising pretreatments will have an effect. Apart from improving dispersion, these oxygen functional groups could be vital links for the cobalt to interact with the activated carbon. The tests on combinations of cobalt and activated carbon (3.1.1) suggested that an interaction between the activated carbon and the cobalt was essential. In fact, the general observation

reported in the literature that nitrate salts were an essential ingredient (when inert calcination atmospheres were used)(1.2.1.4) also supports this postulate. The decomposing nitrate salt will undergo a redox decomposition. If the metal ion is sufficiently stable, then the carbon environment immediately in contact with the decomposing salt would be partially oxidised. Again, this could provide the link between the cobalt and the activated carbon. It was reported that no other salts used were as successful as the nitrate and none of these salts were capable of undergoing a redox decomposition. Where catalysts were synthesized from salts other than the nitrate, it was necessary to calcine the catalyst in a gas containing oxygen at 300-400°C. This treatment would cause mild oxidation of the activated carbon and affect the metal support interaction.

Another important aspect concerning the active sites is the reported thermal instability of the catalysts (Fig. 1.1). This could be the result of either or both of two phenomena: the first is simply that at high temperatures, the cobalt ions will have a tendency to sinter; or secondly, the active sites (some combination of hexaammine, pentaammine, Co^{2+}, Co^{3+}) decompose due to shifted equilibria or reduction in the presence of carbon at high temperature.

4.1.5 Tests of Active Site Hypotheses

The first tests were simpy to oxidise the activated carbon further in the hope of seeing a promoting effect. The method due to Boehm (1966) of oxidising the activated carbon in pure oxygen was used to give a maximum oxidised surface. The effect of this treatment was not very significant when considering total liquid production. Co-OC produced 63g/g compared to the 66g/g of Co-C1hA. However, for the same WHSV the initial conversion was higher and the lifetime shorter. The dimer content was reduced by 2% compared to Co-C1hA. Although this is within experimental error, the trend was consistent. It is possible that the sites were more strongly activated giving both the higher initial conversion and deactivation rate and in addition the longer chain product.

This result, along with the observations of the nitric acid treatments, was considered neither to support nor to contradict the previously stated idea that oxygen functional groups are necessary for an active catalyst. It was conceivable that the activated carbon was already optimally oxidised by its activation procedure. This issue was not clarified by manufacturer specifications. These results did however suggest that the oxygen functional groups were not undersirable.

The role of ash content was examined briefly by pretreatment of the surface with HF. The HF treatment reduced the ash content to almost zero and the activity of the catalyst was reduced. Schultz et al. (1966a) stated that for their system, the sum of CoO and ash must be 15 wt% for optimum activity although they used 13,5 wt % CoO with 0,1 wt % ash. The role played by the ash was not determined. It is possible that there are a limited number of sites on the activated carbon for interaction with the cobalt and that some of these sites were occupied by ash. If the ash content was reduced, it would follow that more active cobalt could be loaded. However, the reduction in activity with ash in this work was puzzling. One possibile explanation is that the cobalt would be more dispersed. This would be detrimental if a two site reaction mechanism occurred for the oligomerization reaction (ie. the reaction takes place between two adsorbed propene molecules).

The second major tests were the synthesis and loading of cobalt hexaammine nitrate onto the activated carbon. This complex was selected for examination because its formation is catalyzed by activated carbon (Bjerrum and McReynolds, 1946) and all of the reactants were available in the double ammoniation synthesis. Of interest was the fact that the number of moles of complex loaded corresponded closely to the 10 wt% Co loading specification of Schultz et al. (1966a). It was believed that the complex was chemisorbed onto oxygen functional groups (as in the mechanism in 1.3.3.1). All interaction sites on the activated carbon would thus appear to be utilised in both catalysts (ie., the catalysts are optimally loaded). It was also considered to be highly significant that the decomposition of the complex took place at virtually the optimal calcination temperature of 275°C according to Schultz et al.

(1966a). Further, the slow decomposition of the loaded complex suggested that some would still be present after several hours. The results of the tests suggest that the resultant species loaded was not the active combination. Further, the ammoniation did nothing to promote this catalyst.

4.1.6 Catalyst Coking and Regeneration

As outlined in 3.1.7, an attempted regeneration of a spent catalyst failed. TG-DTA analysis of the coked catalyst suggested that it was severely coked with long chain hydrocarbons. This agrees with the observations of Schultz et al. (1966a) who extracted heavy polymers of average molecular mass in the range 2000-3000g/mol. It was unlikely that graphitic coke had formed due to the low operating temperature and the lack of cracked products in the liquid and flue gas analyses. If deactivation was solely caused by site blockage, calcination at 180°C under flowing UHPN_2 should have removed a significant percentage of coke (as sugested by thermal analysis, Fig. 3.8) and some activity should have reappeared. Since this procedure did not restore activity, it had to be assumed that some other mechanism caused deactivation. There was no point in attempting to regenerate at higher temperatures because of the thermal instability of the catalyst. The literature proposed regeneration procedures requiring high temperatures and media such as H_2 and NH_3. These were not investigated because it was felt that the entire nature of the catalyst was being changed by such procedures.

4.2 The Cobalt Supported Aluminosilicate Catalysts

Five different supports were tested and as many synthesis procedures were involved. The objectives of this work were: to identify any other systems where cobalt became active for oligomerization at low temperature; to determine whether selectivity changes occurred when cobalt was present in acid catalyzed reactions and finally to determine whether cobalt promoted the acid catalyzed reactions. The selection of synthesis procedures and metal loading percentages were made according

to either well characterised cobalt catalysts reported in the literature or nickel analogues which were known to be active.

The aluminosilicate supports selected covered a wide range of amorphous, clay and zeolite structures and each was considered to be fairly well representative of its class. Two zeolites were chosen because of the growing importance of zeolites in catalysis. In the event of the cobalt being active on these aluminosilicates, the series would have the merit of introducing shape selectivity through steric effects. Conversely, if the cobalt was inactive on its own, its effect on the acid catalyzed reaction could be tested. All of the aluminosilicates catalyze cracking reactions and the formation of branched products. The tendency of cobalt to form linear products (as suggested by the Co-C catalysts) could only be an advantageous effect for the production of diesel.

4.2.1 Silica Alumina

The cobalt silica alumina catalyst (Co-Si/Al) showed low activity when exposed to propene at 50 atm and 70°C. A metal-support interaction had taken place and an active catalyst had been synthesized. It must be pointed out that tha surface area of silica alumina was ca. a quarter of that of the activated carbon. If the same sites were present then a reduced activity would not be surprising. The mechanism is however totally different to that of the Co-C catalyst. This is seen by the switch in product spectrum from dimer to trimer as shown in Fig. 3.21. Since the reaction temperatures were similar, the nature of these active sites must have been different.

The conversion was low when compared to the data of Harms (1987) for the nickel analogue. One experiment was reported where a 11,7 wt% nickel catalyst (supported on the identical support and synthesized by urea decomposition) had a conversion approaching 85% at 80°C and 40 atm with a WHSV of $4,9h^{-1}$. The cobalt catalyst produced a maximum conversion of 20% at a WHSV of $6,2h^{-1}$, a pressure of 50 atm and a temperature of 70°C. The 10°C difference might have been significant. It is known in the literature of silica catalysts (Montes et al., 1984) that the strength

of the metal-support interaction can be markedly affected by the synthesis procedure and by the percentage metal loaded. The homogeneous deposition-precipitation method in the presence of urea was reported to give stronger metal-support interaction than simple impregnation on silica catalysts. It is quite possible that cobalt requires a different synthesis procedure and pecentage loading to become optimally activated.

The product spectra of the Ni-Si/Al and Co-Si/Al catalysts were distinctly different. Little elucidating literature was available on the nature of the sites of the more well researched nickel catalyst. Since the 180°C experiment with Co-Si/Al gave very similar results to those obtained using pure silica alumina, it is possible that at lower temperatures active sites are on the metal crystallites. This is supported by the reported need for good dispersion and the well known metal hydride theory. The extra d electron in the cobalt gives it the possible (III) valence state which the nickel does not have. This has repercussions on the strengths of adsorption and the number of available co-ordination sites for reactant molecules. Hence the reaction mechanism would be different. A comparative investigation of the interaction of the metals with the support could reveal why cobalt is a dimerising catalyst on activated carbon but a trimerising catalyst on silica alumina and for that matter why nickel is a dimerising catalyst on silica alumina and is inactive on activated carbon.

It has been suggested above that the cobalt impregnated onto the silica alumina did not effect the activity of the catalyst at 180°C. Fig. 3.21 shows that the Co-Si/Al liquid spectrum at 180°C was lighter than the pure silica alumina liquid spectra at the same temperature. It is however, clear from Fig. 3.19 that the Co-Si/Al product spectrum shifted to approximately the same distribution as unmodified silica alumina as conversion dropped. No significant comment could be made regarding the effect of cobalt on the lifetime of silica alumina.

The molybdenum modified catalyst was clearly different. No activity was observed below 100°C. Conversion to metathesis products was low although the WHSV was relatively high. The presence of the silica and its

resultant acidity in conjunction with the higher WHSV, could explain the lower activity of this catalyst when compared to the data reported by Pines (1981).

Pines (1981) suggests that cobalt plays the role of a promoter in this metathesis reaction and that molybdemun is the essential component. Throughout the work of this thesis, no significant ethene production was detected for any of the other cobalt catalysts. Since ethene is always a metathesis product where propene is present, it was concluded that no metathesis function occurred elsewhere.

4.2.2 SMM

The cobalt ion exchanged into SMM did not give any positive effects at either 70°C or 130°C. The activity of the catalyst was reduced and the liquid spectra remained unchanged. The reduction in conversion was believed to be simply the result of a loss of acidity. Attempts to support this point via ammonia Temperature Programmed Desortion (TPD) techniques were not successful because the adsorption of ammonia onto 0,5g of catalyst at 100°C was so low that desorption peaks could not be detected by the TPD apparatus.

The question arises as to whether the catalyst parameters chosen where meaningful. Firstly, Jacobs (1987) found that both 0,05 wt% and 0,5 wt% nickel ion exchanged SMM had promoted activities with initial rates of liquid production almost doubled (at 130°C) although lifetime was reduced. The reaction temperature of 130°C was appropriate since cracking became significant at 190°C. Jacobs (1987) also reported that both of the above nickel catalysts were active at 90°C, giving LP of 2,3g/g·h at a WHSV of $8h^{-1}$. Speculation as to the role of nickel in these catalysts was that it was capable of forming an active hydride species (at 90°C) analogous to the homogeneous catalytic hydride species. The lower homogeneous activity of the Co-H analogue could explain why the Co-SMM catalysts were inactive at low temperature. At 130°C, it was believed that the nickel ions promoted the activity of the

acidity remaining after ion-exchange. The electronic effect of the cobalt ions either had no effect or a suppressing effect on the acidity.

4.2.3 Zeolity Y

The acidity of protonated zeolite Y was considered to be too strong to be an effective catalyst. High deactivation rates suggested both the formation of long chain hydrocarbons and graphitic coke and increased difficulty for desorption of product from the strong sites. Ion exchange of cobalt into the protonated form did not improve the lifetime. Intra-particular mass transfer limitations were a possible cause of the improvement in performance when pellets were used.

The low and short lived activity of Co-LZY52 at 180°C was surprising. The high trimer content (58%) was reminiscent of that due to the Co-Si/Al catalyst when run at 70°C. The activity of the latter was established to be the result of the presence of cobalt. Although the temperatures were vastly different, it would appear that this activity was in fact due to the presence of cobalt. If stray acidity associated with the zeolite had been present, then the product spectra would presumably have been closer to that of LZY82 ie. a 35% trimer content. This result possibly suggests that far higher temperatures are needed to produce an active cobalt site for propene oligomerization. The short lifetime indicates that the more extreme conditions may be detrimental.

The ammoniated version of the above catalyst (Co-LZY52) was active at 88°C. The low dimer content (7%) suggested that a different mechanism was operating to that of the Co-C catalyst. The liquid spectrum was remarkably similar to that of LZY52 pellets operated at 145°C and the two catalyst had similar conversion levels. The ammonia treatment could easily have resuted in some ion exchange of Na^+ ions for NH_4^+ ions. If these had decomposed into acid sites, this would explain why the liquid product spectra were similar. However, it was questionable what the extent of deammoniation would be at 260°C and partial vacuum of 3 mmHg.

4.2.4 NH_4^+-ZSM-5

The work with NH_4^+-ZSM-5 showed that no bifunctionality was introduced either by impregnation or by ion exchange of cobalt into this zeolite. The activity of the zeolite was clearly affected. It was suspected that the poor performance of the 4,5 wt% impregnated catalyst was due to both pore and site blockage by cobalt oxide crystallites on the outer surface of the zeolite. The similarly synthesized catalyst characterised by Stencel et al. (1983) had 1,4 wt% Co ion exchanged into the zeolite and the remainder located on the external surface. This explanation was supported by the fact that simply washing the catalyst (but leaving 1,1 wt% of presumably ion exchanged Co) produced a catalyst of greater activity. A similar result was obtained for the nickel analogue (Schwarz, 1987).

The performance of the ion-exchanged catalyst was good considering the fairly large degree of ion exchange which had taken place. The lack of significant activity at 180°C suggested that the strongest sites may have been removed by ion exchange - higher temperatures were necessary to cause the remaining sites to become active. This could also be due to a negative electonic effect caused by the introduction of cobalt. At 280°C, the Cracking Index revealed that cracking was far less prevalent in the cobalt catalyst as opposed to the control. Again this could simply be due to a loss of the strongest acid sites. The ion exchange of any inert metal should thus cause a similar effect. The consequence of reduced cracking on lifetime was not measured although it was suspected that lifetime would be improved since the cracking reaction which is associated with coking, was retarded. The reduction of light cracked products would be a clear advantage when trying to produce diesel.

4.3 Concluding Remarks

A large number of cobalt catalysts were synthesized and tested for propene oligomerization activity. The activated carbon supported catalysts were found to be extraordinarily active - one version (Co-

C1hA) gave an initial liquid production of 10,9g/g·h with a conversion of 85% at a propene WHSV of 12,8h^{-1}. All of these carbon supported catalysts yielded low lifetimes and steady state conditions were never observed. It was argued that the differences with the data of Schultz et al. (1966a) were not the result of experimental procedures but rather were the result of the nature of the specific catalyst synthesized. Hill (1970) in his patent on regenerating Co-C catalysts observed that "cobalt/carbon catalysts tend to lose their activity quite quickly and it is desirable to be able to restore their activity readily." Only Schultz et al. (1966a) have been successful in obtaining long lifetimes.

The following conclusions were drawn from the present work:

i) The double ammoniated Co-C catalyst is unique in its high selectivity to dimeric product.

ii) Ammonia treatments markedly improved the activity of the Co-C catalysts.

iii) Untreated Co-C catalysts showed slight activity. This activity was not observed on an inert alumina support. Low activity was observed on a silica alumina support but the product spectra suggested that a totally different mechanism and sites were involved.

iv) A direct interaction between cobalt and the carbon support was essential to produce a dimerizing catalyst.

v) The nature of the activated carbon used was critical to catalyst activity and selectivity.

vi) Nitric acid pretreatments of the activated carbon were found not to improve the catalyst performance.

vii) HF pretreatment of the activated carbon did not improve activity although it was recognised that a higher cobalt loading might have been necessary.

viii) The role of the ammonia pretreatment would seem to be primarily to improve cobalt adsorption and dispersion.

ix) The role of the ammonia in the post-ammoniation treatment remained uncertain.

x) The $Co(NH_3)_6(NO_3)_3$ complex was found not to be the active site precursor when loaded onto the activated carbon via aqueous solution.

xi) An optimal post-ammoniation contact time of ca. 1h was found to exist for this catalyst system.

xii) A reduced selectivity to dimer was associated with a higher deactivation rate.

xiii) This work supported the previously reported observations that lifetime was reduced by high operation temperatures and O_2 and H_2O in the feed.

xiv) The spent catalyst could not be regenerated by heating at 180°C in flowing N_2.

By contrast, the cobalt aluminosilicate catalysts were not particularly active and no combination tested gave the dimerizing ability or activity of the activated carbon supported catalysts. The conclusions relating to these catalysts were as follows:

i) Although the Co-Si/Al catalyst gave only a 20% conversion at 70°C and a WHSV of $6,2h^{-1}$, if was felt that the catalyst parameters had not been optimised. This system clearly gave an active site which could possibly be significantly improved.

ii) The role of cobalt would appear to be that of a promoter as no propene metathesis products were observed in any of the other catalyst systems.

iii) The protonated form of zeolite Y deactivated rapidly and was thus not considered for further work.

iv) A cobalt ion-exchanged NaY catalyst showed slight activity when treated with ammonia and activated at 260°C under flowing N_2. The cause of this activity remained uncertain. A better understanding of the role of ammonia in activating the Co-C system could have clarified this issue.

v) Cobalt ion-exchanged into SMM gave no positive effects of either increasing activity or causing a selectivity change under the conditions tested.

vi) Cobalt impregnated onto NH_4^+-ZSM-5 reduced the activity of the acid catalyzed reaction. This was most probably due to surface and pore blockage.

vii) Cobalt ion-exchanged into NH_4^+-ZSM-5 gave no synergistic effects. Selectivity to heavier products was improved by a reduction in cracking. This reduction was believed to be the result of the strongest acid sites being lost through ion-exchange. It was uncertain whether this result would have been obtained by the use of any inert metal.

REFERENCES

Adams, C.T. amd Brandenberger, S.G. (1969), J. Catal., 13, 360-3.

Addy, L.E. and Hill, T. (1968a), British Patent 1102298.

Addy, L.E. and Hill, T. (1968b), British Patent 1123766.

Argauer, R.J. and Landolt, G.A. (1972), US Patent 3702886.

Arnoldy, P. and Moulijn, J.A. (1985), J. Catal., 93, 38-54.

Banks, R.L. and Bailey, G.C. (1964), Ind. Eng. Chem. PRD, 3(3), 170-3.

Bartholomew, C.H. and Boudart,M. (1972), J. Catal., 25, 173.

Bjerrum, J. and MacReynolds, J.P. (1946), Inorg. Syn., 2, 216.

Boehm, H.P. (1966), Adv. in Catal., 16, 309-330.

Bond, G.C. (1962), "Catalysis by Metals", Academic Press, NY.

Burggraph, L. and Leyden, D.E. (1982), J. Catal., 78, 360-79.

Chang, C.D. and Silvestri, A.J. (1979), J. Catal., 47, 247.

Cheney, H.A. (1946, a), US Patent 2407813.

Cheney, H.A. (1946, b), US Patent 2407814.

Cheney, H.A., McAllister, S.H.,Fountain, E.B., Anderson, J. and Peterson, W.H. (1950), Ind. Eng. Chem., 42, 2580.

Cookson, J.T. (1978), "Carbon Adsorption Handbook", Ann Arbor Science Inc., 241-279.

Coughlin, R.W. (1969), Ind. Eng. Chem. P.R.D., 8, 12.

Coulter, A.K. and Clemens, L.N. (1964), J.Phys. Chem., 68, 651.

Clark, A. (1953), Ind. Eng. Chem., 45, 1476.

Dhere, A.G. and De Angelis, R.J. (1985), J. Catal., 92, 145-154.

Dwyer, F.P. and Sargeson, A.M. (1960), Nature, 187, 1022-1023.

Dzwigaz, S., Haber, J. and Romotowski, T. (1983), Zeolites, 3, 134-138.

Egerton, T.A., Hagen, A., Stone, F.S. and Vickerman, J.C. (1972), J. Chem. Soc. Faraday I, 68, 723.

Eidus, Ya T., Guseva I.V. and Slovetskaya, K.I. (1960), Izvestiya Akademii Naul SSSR, Otdelenie Khemicheskikh Nauk, No.2, 337-343.

Fasol,R.E. (1983), M.Sc. Thesis, University of Cape Town.

Fraissard, J. (1980), Catal. by Zeolites, Elsevier Scientific Publ.

Fel'blyum, V.SH. and Baranova, T.I. (1971), Z. Org. Kimii, 7, 2257.

Fletcher, J.C.Q. (1984), PhD. Thesis, University of Cape Town.

Gil-Llambias, F.J. and Escudey-Castro, A.M. (1983), J. Catal., 83, 225-28.

Hammershoi, A., Geselowitz, D. and Taube, H. (1984), Inorg. Chem., 23, 979-982.

Harms, S.M. (1987), MSc. Thesis, UCT.

Healey, F.M., Yu, Yung-Fang and Chessick, J.J. (1955), J. Phys. Chem., 59, 399.

Hill, T. (1966), British Patent 1151266.

Hill, T. (1970), British Patent 1185172.

Hogan, J.P., Banks, R.L., Lanning, W.C., and Clark, A. (1955), Ind. Eng. Chem., 47, 4.

Howe, R.F. and Lunsford, J.H. (1975a), J. Phys. Chem., 79.

Howe, R.F. and Lunsford, J.H. (1975b), J. American Chem. Soc., 97, 5156-9.

Imai, H. and Uchida, H. (1965), Bull. Chem. Soc. Japan, 38, 925.

Ion, D.C. (1976), "Availability of World Energy Resources: First Supplement", Graham and Trotman.

Jablonski, H.M., Mulak, J. and Romanowski, W. (1977), J.Catal., 47, 147-158.

Jacobs, L.L. (1987), MSc. Thesis, UCT.

Jager, B. (1978), Fischer-Tropsch Synthesis, Spring School in Coal Conversion, Rand Afrikaans University.

Jones,J.R. (1971), J.Chem.Soc., 1117-1124.

Kipling, J.J. (1956), Quart. Revs., 10, 1.

Laine, N.R., Vasola, F.J. and Walker, P.L.Jr (1963), J. Phys. Chem., 67, 2030.

Mahan, B.H. (1972), "University Chemistry", 2nd Ed., Addison-Westley.

McNair, H.M. and Bonelli, E.J. (1968), "Basic Chromatography", 5th Ed., Varian.

Meier, J.A. and Hill, L.W. (1974), J.Catal., 32, 80-87.

Miyamoto, A., Chi, T. and Murakami, Y. (1984), J. CAtaal., 88, 256.

Mol, J.C. and Moulijn, J.A. (1975), Adv. Catal., 24, 131-171.

Montes, M., Penneman De Bosscheyde, Ch., Hodnett, B.K., Delannay, F., Grange, P. and Delmon, B. (1984), Applied Catal., 12, 309-330.

Morikawa, K., Shirasaki, T. and Okada, M. (1969), Adv. in Catal., 20, 128-130.

Mureinik, R.J. (1977), J.Catal., 50, 56-63.

Occelli, M.L., Hsu, J.T. and Galya, L.G. (1985), J. of Molecular Catalysis, 32, 377-390.

Peuchert, M. and Linden, G. (1984), 8th International Congress on Catalysis, 2, 11-135.

Pincock, R.E., Johnson, W.M. and Haywood-Farmer, J. (1976), Can. J. Chem., 54, 548-554.

Pines, H. (1981), "The Chemistry of Catalytic Hydrocarbon Conversions", Academic Press, NY.

Pope, D., Walker, D.S. and Moss, R.L. (1977), J. Catal., 47, 33-47.

Ramser, J.H. and Hill, P.B. (1958), Ind. Eng. Chem., 50, 1.

Richardson, J.T. and Dubus, R.J. (1978), J. Catal., 54, 207.

Schlessinger, G.G. (1967), Inorg. Syn., 9, 160.

Schuck, J.M., Groves W. and Schultz R.G. (1967), US Patent 3317628.

Schultz, R.C., Schuck J.M. and Wildi B.S. (1966a), J.Catal., 6, 385-396.

Schultz, R.C., Engelbrecht R.M., Moore R.N. and Wolford L.T. (1966b), J.Catal., 6, 419-426.

Schultz, R.C. (1967a), US Patent 3333016.

Schultz, R.C. (1967b), J.Catal., 7, 283.

Schuster, C. (1932), J. Electrochem., 38, 614.

Schwarz, S. (1987), Unpublished work, UCT.

Smisek, M. and Cerny, S. (1970), "Active Carbon", Elsevier Publishers N.Y.

Stencel, J.M., Rao V.V.S., Diehl, J.R., Rhee, K.H., Dhere, A.G. and DeAngeles, R.J.(1983), J.Catal., 84, 109-118.

Studebaker, M.L., Huffman, E.W.D., Wolfe, A.C. and Nabors, L.G. (1956), Ind. Eng. Chem. 48, 162.

Takahashi, K. Sasaki, O., Aomura, K. and Ohtsuka, H. (1969), Hokkaido Daigaku Kogakubu Kenkyu Hokoku, 53, 201.

Tomita, A., Mori, S. and Tamai, Y. (1971), J.Catal., 23, 141-145.

Tomita, A. and Tamai, Y. (1971), J. Phys. Chem., 75, 649-654.

Topsoe, N. and Topsoe, H. (1982), J. Catal., 75, 354-74.

Tsuruya, S., Miyamota, H., Sakai, T. and Masai, M. (1980), J.Catal., 64, 260-271.

Van Dillen, J.A., Geus, J.W., Hermans, L.A.M. and Van Der Mijden, (1976), Proc. 6th Int. Cong. Catal., B7.

Ward, J.W. (1971), J.Catal., 22, 237-244.

Walker, P., Austen, L. and Tietjen, J. (1965), "Chemisty and Physics of Carbon", 1, 327.

Walker, P.L.Jr and Janov, J. (1968), J. of Colloid and Interface Sci., 28, 449.

Wiese, H.K. (1977), US Patent 4029601.

Wilshier, K.G., Smart, P., Western, R, Mole, T. and Behrsing, T. (1987), Applied Catal., 31, 339-59.

Wright, A.C., Granquist, W.T.and Kennedy, J.V. (1972), J.Catal., 25, 65.

Yoshida, S., Nakajima,M., Naito,K., Koshimidzu, Y. and Tarama, K. (1974), Bull. Ins Chem. Res., Kyoto Uni., 52, 567-78.

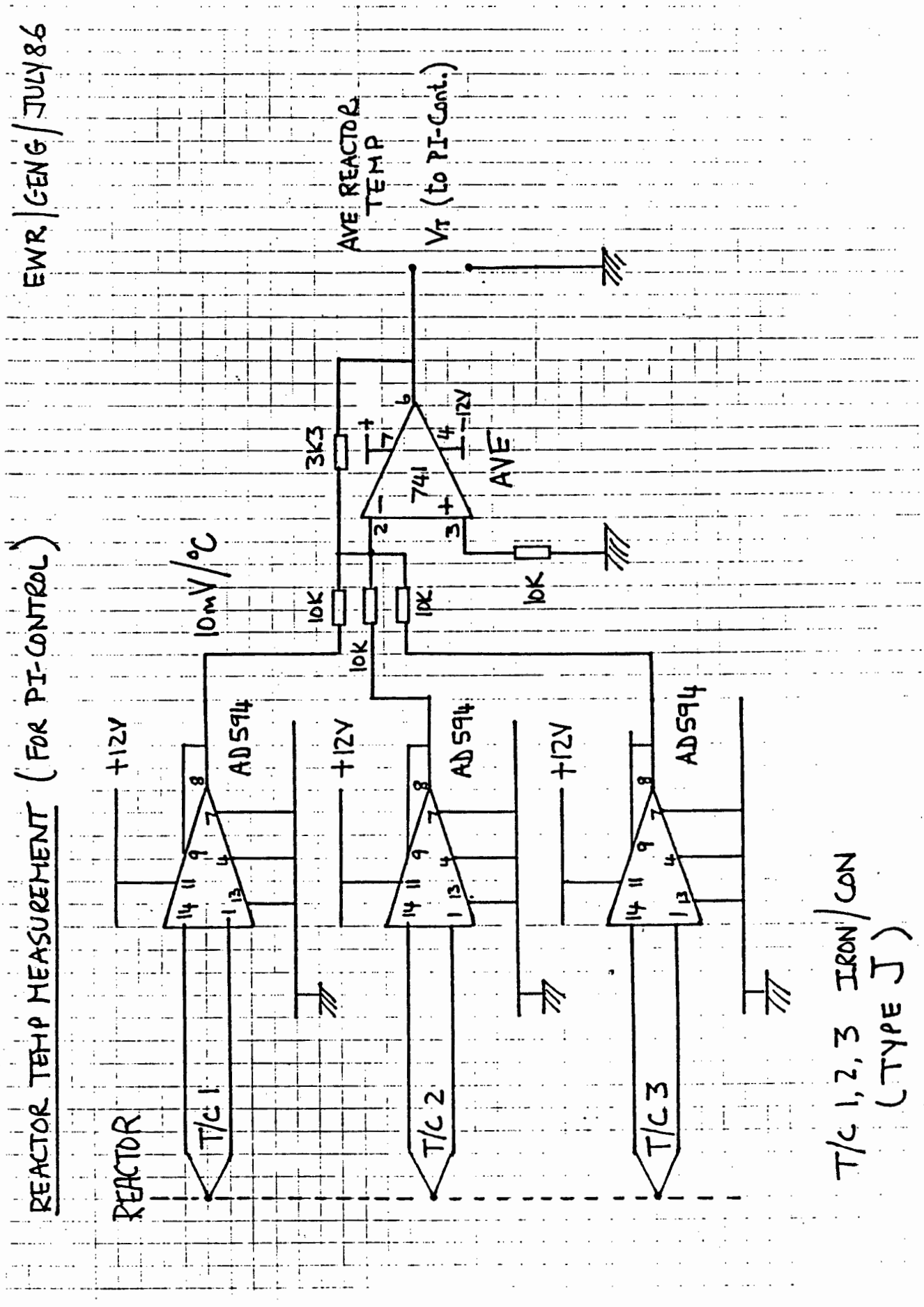
APPENDIX

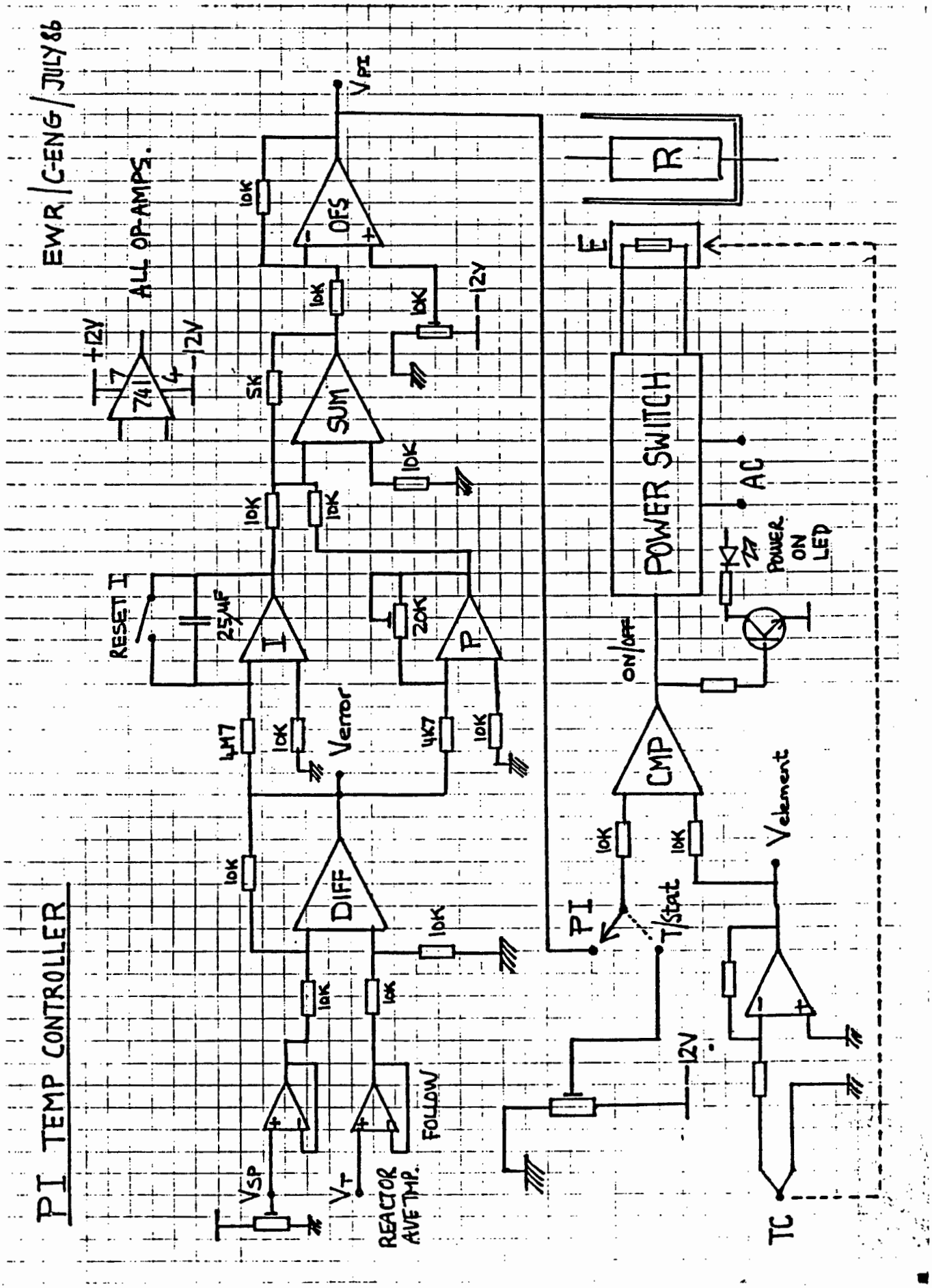
i) P.I. Controller Design

The PI controller was chosen as a suitable controller because of the usual advantages of eliminating offset errors between the measured variable and the setpoint; and because of the more stable control action as opposed to a PID controller. The response time of the PI controller was expected to be slow but this was considered to be acceptable because of the slow dynamics of catalyst deactivation. In theory, only the loss of heat through decreasing reaction should cause the reactor temperature to change. In this case, ambient temperature variations during long experiments could also cause temperature variation.

A combination of operational amplifiers was used to build the controller. It was recognised that computer control would have given greater flexibility in control actions. The analogue system had the distinct disadvantage that temperature ramping had to be done manually. Not only was this disadvantageous for the operator but also reproducibility betwee+n calcinations was made more difficult to achieve. Nevertheless, the analogue system had the merit of being inexpensive and could be relatively quickly installed.

The electronic circuitry is shown on the following two pages. The first figure shows the arrangement for measuring and averaging the thermowell thermocouple signals. As stated in section 2.2.1, special operational amplifiers with with cold junction correction (AD594) were used to convert the millivolt thermocouple signal into a signal of the order of 1-5V. This value was also used via a multimeter as the temperature display. The reading producted an offset which increased with increasing temperature. A manufacturer supplied calibration chart was used to correct the reading accordingly. The second figure shows the PI controller configuration. The curcuit took the difference between the setpoint and the averaged reactor temperature. This difference was


EWR/CENG/JULY 86
REACTOR TEMP MEASUREMENT (FOR PI-CONTROL)
AVE REACTOR TEMP
V_T (to PI-Cont.)
3K3
741
AVE
+12V
-12V
10K
10mV/°C
AD594
REACTOR
T/C 1
T/C 2
T/C 3
T/C 1, 2, 3 IRON/CON (TYPE J)


PI TEMP CONTROLLER
EWR/C-ENG/JULY 86
ALL OP-AMPS.
+12V
741
-12V
VPI
OFS
SUM
I
P
DIFF
CMP
Vemor
Velement
RESET I
25μF
20K
4K7
10K
5K
+12V
-12V
VSP
VT
REACTOR AVE TMP.
FOLLOW
R
F
POWER SWITCH
AC
POWER ON LED
ON/OFF
PI
T/Stat
TC

integrated and added to a multiple of the error (viz. the proportional term). The combined signal was the setpoint for a simple comparator (CMP) which behaved like a thermostat.

ii) G.C. Analysis of C_6 Isomers

The megabore column was used in an attempt to separate the C_6 isomers in the product of the cobalt-carbon catalysts. A standard containing trace quantities of C_6 isomers in an octane solvent was made up. Separations were attempted at temperatures in the range 15°C to 40°C. A significant improvement was attained by the reduction in temperature from 40-15°C. This reduction was achieved by installing a glycol cooling coil in the G.C. oven. This coil was problematic when it was necessary to condition the column or to drive of the octane solvent at ca. 80°C. At this low temperature, the peaks broadened. The group of isomers described in section 2.4.3 as having a peak with two shoulders became even less clear through this peak broadening. Clearly the column was not capable of separating this group.

Another problem encountered with this attempt was that of column linearity. Since only limited quantities of the standard solutions were available. it was necessary to dilute them down to levels of 1% and less. When the pure product was run for comparison with the standards, the peaks came out at totally different times. This meant that even the single peaks could not be positively identified.

A sample of the product spectrum generated by the megabore for a Co-C catalyst is shown on the following pages. The oligomer groupings are clearly visible. The two groups of isomers referred to in 2.4.3 are the peaks at 4,72 min and 5,87min respectively. On making a 1:3000 dilution of the product with octane, the shoulders became visible in these peaks. Clearly several isomers were present in these peaks. This dilution method was not considered at be a satisfactory analytical procedure because of the volatile nature of the hexene fraction.

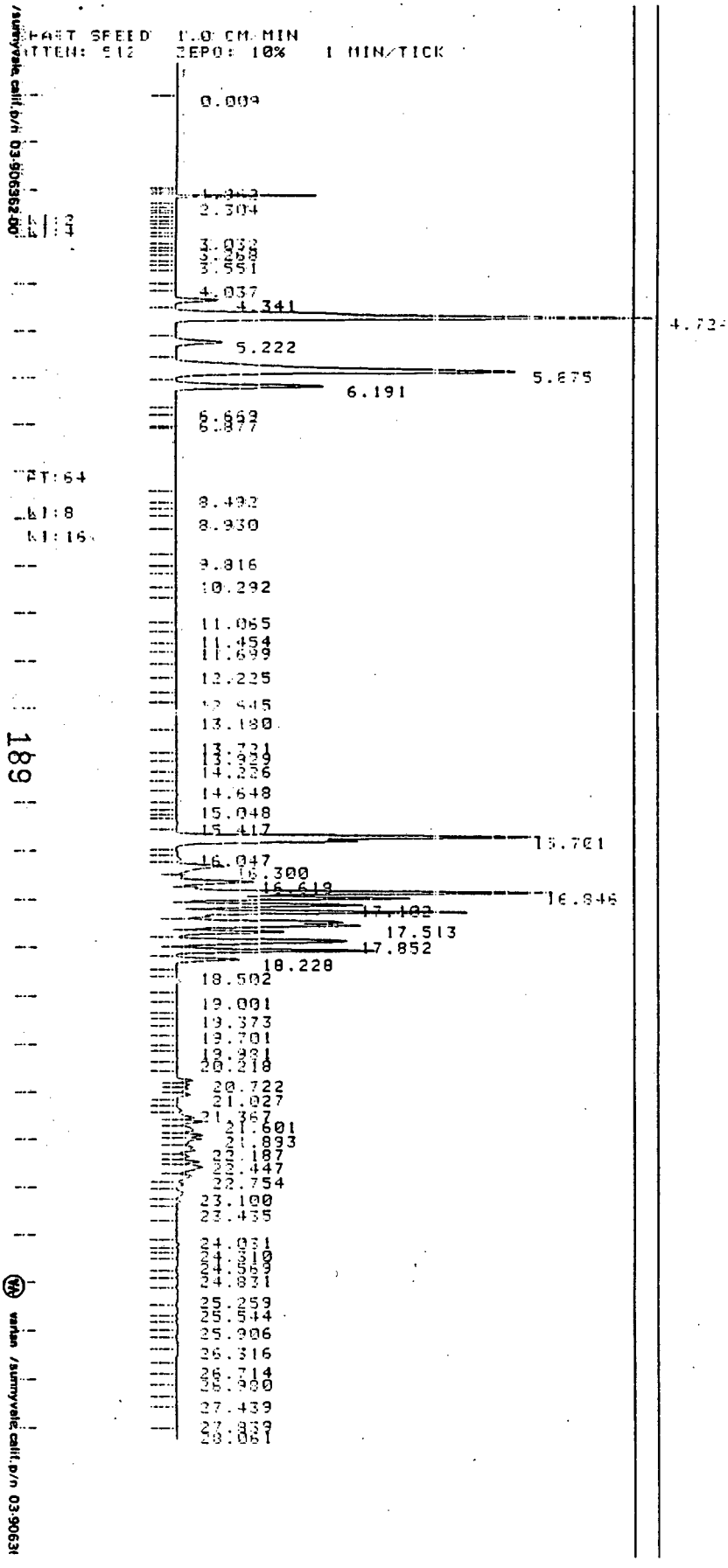


CHART SPEED 1.0 CM/MIN
ATTEN: 512 REPO: 10% 1 MIN/TICK
0.009
2.304
3.032
3.551
4.037
4.341
4.724
5.222
5.675
6.191
6.669
6.877
8.492
8.930
9.816
10.292
11.065
11.454
11.699
12.225
13.180
13.731
13.929
14.226
14.648
15.048
15.417
15.701
16.047
16.300
16.619
16.846
17.102
17.513
17.852
18.228
18.502
19.001
19.373
19.701
19.931
20.218
20.722
21.027
21.367
21.601
21.893
22.187
22.447
22.754
23.100
23.435
24.031
24.310
24.569
24.831
25.259
25.544
25.906
26.316
26.714
26.900
27.439
27.839
28.061

TITLE: COMPOSITION DATA 23:39 21 MAY 87

CHANNEL NO: 2 SAMPLE: C00CSPAS1 METHOD: PAULB

PEAK NO	PEAK NAME	RESULT MASS %	TIME (MIN)	AREA COUNTS	SEP CODE
		2.7	2.117	147717	BV
		0.0	3.432	1093	VV
		1.9	4.341	106532	VV
		32.8	4.724	1828390	VV
		2.8	5.222	154353	VV
		32.2	5.875	1792310	VV
		8.7	6.191	485308	VV
		3.5	15.701	192490	VV
		0.0	16.148	1526	T
10		0.4	16.300	24221	VV
11		0.5	16.618	30306	VV
12		2.6	16.846	145200	VV
13		1.2	16.951	66562	VV
14		1.2	17.102	68553	VV
15		1.7	17.242	95574	VV
16		2.0	17.513	109392	VV
17		0.6	17.662	35340	VV
18		1.5	17.852	82554	VV
19		1.0	18.043	55928	VV
20		0.3	18.228	18360	VV
21		0.0	18.671	2050	VV
22		0.1	20.722	5355	VV
23		0.1	20.832	4519	VV
24		0.1	20.892	4069	VV
25		0.1	21.027	4726	VV
26		0.0	21.367	2048	VV
27		0.1	21.509	6304	VV
28		0.2	21.601	9506	VV
29		0.2	21.765	9411	VV
30		0.2	21.893	9271	VV
31		0.2	21.966	10308	VV
32		0.2	22.187	11561	VV
33		0.1	22.334	4364	VV
34		0.1	22.447	7224	VV
35		0.3	22.556	14567	VV
36		0.1	22.754	7230	VV
37		0.0	22.909	2392	VV
38		0.1	23.100	3962	VV
39		0.0	23.276	1359	VV
40		0.0	24.183	1012	VV
41		0.0	24.569	1389	VV
42		0.0	24.971	1126	VV
43		0.0	25.259	2223	VV
44		0.0	26.316	1098	VV
45		0.0	26.368	1199	VV
TOTALS:		99.8		5573340	

MULTIPLIER: 1.00000